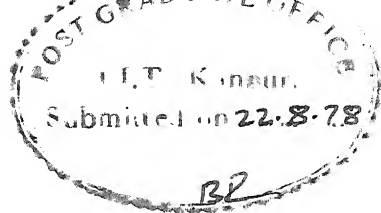


INVESTIGATION ON THE USE OF COAL FOR REMOVING MERCURY FROM WATER

**A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY**

**By
M. P. PANDEY**

**to the
DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
AUGUST, 1978**

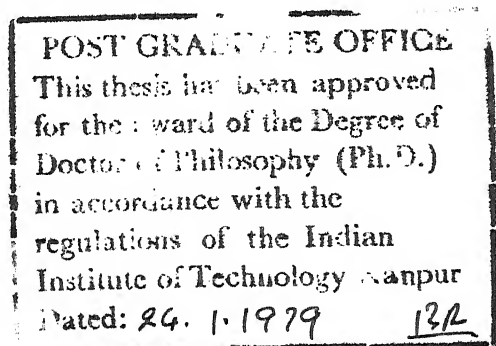


CERTIFICATE

Certified that the work presented in this thesis entitled "Investigation on the Use of Coal for Removing Mercury from Water" by Sri M.P. Pandey has been carried out under my supervision and it has not been submitted elsewhere for a degree.

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INVESTIGATION ON THE USE OF COAL FOR REMOVING MERCURY FROM WATER

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Recent awareness about the occurrence and transport of mercury in aquatic environment and the toxic effects of mercury ingestion have led to several studies on mercury removal from water employing activated carbon or ion-exchange resins. Use of proteinaceous materials such as hair, wool, etc. has also been explored. In spite of their effectiveness, activated carbon and ion-exchange resins are rather expensive. These coupled with the recent studies on the use of coal in water and wastewater treatment led to the present investigation. The objective of the present study was to investigate the potential of coal in removing mercury from water and wastewater.

Giridih bituminous coal was selected for the present study on mercury removal through a screening test involving several bituminous coal samples. Removal of inorganic mercury by the Giridih coal was investigated in laboratory systems using batch sorption tests and column studies. Batch sorption kinetics were described by a first order reversible reaction and sorption equilibria by the Freundlich equation. Mercury sorption was temperature dependent and reduced with increase in pH. The average values of heat of sorption and activation energy were

0.91 and 8.39 kcal/mole, respectively. The ultimate equilibrium mercury sorptive capacity of Giridih coal (Gm 357 μm) at pH 6.2 was observed to be 11 mg/g at 31-33°C. Sorption was also influenced by the chemical environment and the rate increased with increase in mercury concentration. Chemical pretreatment of coal like nitric acid oxidation, sulfonation, and sulfurization improved sorption efficiency. Sorption kinetics data and the effect of sorbent size on the rate of mercury sorption led to the belief that mercury sorption on coal was an intraparticle transport phenomenon. Desorption and regeneration data indicated an ion-exchange nature of the sorption reaction apart from possible contribution of even stronger interactions, e.g., hydrogen bonding and chemisorption. A discussion on the possible interaction between mercury and the surface functional groups on coal has been presented using evidence from infrared spectral studies and information available in the literature.

The second phase of the investigation was devoted to the downflow coal column studies to explore the practical aspects of mercury removal from water and wastewater. The input mercury levels were selected in the range of 10-2,000 $\mu\text{g/l}$ to represent mercury concentrations of natural water and wastewater. When mercury (10 $\mu\text{g/l}$) was present with turbidity, alum coagulation followed by sedimentation preceded column operation and removed about 20 percent of the mercury. The column effluent mercury concentration was 1.0-1.5 $\mu\text{g/l}$ at a flow rate of 6.4 ml/min.

Mercury (10 $\mu\text{g/l}$) in turbidity-free water was reduced by 60 and 80 percent at flow rates of 12.8 and 6.4 ml/min, respectively. The coal columns were effective for a substantial period of time without any need for regeneration or replacement. It was demonstrated that higher initial concentration of mercury (400-2,000 $\mu\text{g/l}$) could be reduced to any desired level by employing coal columns in series. It appears that bituminous coal is effective in removing mercury from water and wastewater and a coal based process may emerge as a cheap alternative to activated carbon and ion-exchange resins.

I. INTRODUCTION

As population and industry expand, the water needs of our society are becoming critical. Exacting demands are being made upon existing water resources to meet the requirements of a highly industrialised society. These demands will mount in future as continuing population expansion and technological advancement lead to both more extensive and intensive use of the available water resources and ultimately to the degradation of water quality. Much of the water currently available to a large segment of the society has been subjected to previous use. Multiple reuse of water is going to be not-too-distant a phenomenon in urban India. To alleviate the water shortage, multiple reuse of water has already become a necessity in many highly industrialised areas. Evidently, as reuse practice increases more stringent requirements will be placed on the treatment of water and wastewater and more effective removal of contaminants will be required.

Mercury is a naturally occurring element that is normally found in minerals, rocks, soil, water, air, plants and animals. It is one of the contaminants reaching natural bodies of water from these sources. Apart from this natural background level of mercury in almost all surface and ground waters, there are man-made sources discharging mercury into these waters. As mercury is highly toxic even at very low concentration, any further addition to the already existing background may be considered a threat to man and his environment. A recent awareness regarding mercury in the environment

has been precipitated by serious mercury poisoning episodes in Japan (Kiyoura, 1970), Sweden (Westoo, 1969) and Iraq (Haq, 1963). The Minamata bay (Japan) incident which occurred in 1953, is the first reported case of mercury pollution in the aquatic environment and caused death or permanent disability of 111 people. The most serious incident of man-made mercury poisoning occurred in Iraq in 1972 (Clarkson, 1972) and this disastrous blunder caused loss of 5,000 to 50,000 human lives and permanent disability of over 100,000 people.

The occurrence and transport of mercury in aquatic environment and its toxic effects have led to several studies on mercury removal from water and wastewater employing sorbents like activated carbon and ion-exchange resins. Use of proteinaceous materials such as hair, wool etc. have also been explored. In spite of their effectiveness activated carbon and resins are rather expensive. These coupled with the recent studies on use of coal in water and wastewater treatment led to the present investigation.

The present work was undertaken in order to evaluate the potential of coal as a sorbent for removing mercury from water and wastewater. Apart from conducting the basic experiments for understanding the mechanism of mercury removal by coal, practical aspects of the process were also studied. Various parameters that may affect the process were also evaluated.

II. PRESENT STATE OF KNOWLEDGE

A. Mercury

1. General

Mercury was one of the first metals known to man. There is evidence that its discovery dates back to atleast the eighth, and possibly the sixteenth century B.C. Mercury was mentioned by Aristotle in his Meteorology and Deanima of approximately 300 B.C. The great Arab physicians used mercury compounds as medicine as early as sixth century B.C. (Engel, 1967). Paracelsus (1493-1541), the founder of modern chemotherapy, introduced the use of mercury for the treatment of syphilis. Some mercury compounds are still being used effectively to treat various infections and disorders.

Mercury is a naturally occurring element that is normally found in minerals, rocks, soil, water, air, plants and animals. The ubiquitous nature of mercury is due, in large part, to the high vapour pressure of the element and its compounds. Mercury can be divided into two major categories, the first, inorganic category contains the widely recognised elemental silvery liquid metal as well as a host of compounds wherein the mercury is present in one of its two most common forms, either as a mercurous ion (Hg^+) or mercuric ion (Hg^{++}). The second category containing organic mercury includes chemical compounds which contain carbon atoms covalently bound to a mercury atom. These relatively new mercury compounds were introduced in the increasing numbers after

the turn of the century. These inorganic and organic mercury compounds are to be considered a threat to man and his environment for their toxic properties.

The toxic properties of mercury compounds have also been known for a long time. Napoleon, Ivan the Terrible, and Charles II of England are suspected of having died of mercurial poisoning (Goldwater, 1971). Mercury and its compounds are cumulative toxins and in rather small quantities have shown to be detrimental to most forms of life (Smith, 1972). A recent awareness regarding mercury in the environment has been precipitated by serious mercury poisoning episodes in Japan (Kiyoura, 1970), Sweden (Westoo, 1969) and Iraq (Haq, 1963). The Minamata bay incident, which occurred in 1953, was the first known modern case of mercury pollution in the aquatic environment and caused the death or permanent disability of 111 people. The primary source of this pollution was an alkylmercury which was found in the effluent of a polyvinyl chloride plant. In the late 1950's other cases of mercury poisoning were found in Pakistan, Iraq and Guatemala (Jalali and Abbasi, 1971; Haq, 1963 and Ordonez et al., 1966). The first serious incident of man-made mercury poisoning occurred in Iraq in 1972 (Clarkson, 1972). The effect of this disastrous blunder caused loss of 5,000 to 50,000 lives and permanent disability of over 100,000 people (possibly 500,000). In 1970 alarm rose to a dramatic pitch in North America when there were many reports about the occurrence of high levels of mercury in

fish from various lakes and streams in both Canada and the U.S.A. (Goldwater, 1971). In India, the reported level of mercury in few samples of fish found near the Bombay coast was 500 ng/g, which is the maximum allowable concentration laid down in Sweden (Tejam and Haldar, 1975).

2. Mercury in the Environment

Both man and nature contribute to the contamination of our environment with mercury. Nature's contribution to the problem is due to some unique properties of the element, the way it is found in the nature and its ability to recycle readily. The compounds of mercury, like many other chemical compounds are dispersed throughout rocks, soil, air, water and living organisms by a complex system of physical, chemical and biological control.

a. Sources

Estimates of both natural and anthropogenic sources of mercury are subject to considerable error. Level of mercury in environmental samples as ice from Greenland are extremely low and close to the limit of sensitivity of the analytical methods. These low values are then converted by large multiplication factors (annual total global rainfall, $5.2 \times 10^5 \text{ km}^3$) so as to obtain values for the global sources and mercury turnover. Coal and oil, an important anthropogenic source of mercury vary highly in their mercury contents. The variation of mercury content in crude oil is of the order of 1000 fold and it is of even higher order in the case of coal from different sources (D'Itri, 1972). Estimates

of industrial production and consumption of mercury are subject to vagaries because of concern over mercury pollution in recent years. However man-made sources are of considerable importance in terms of local environmental contamination.

i. Natural Occurrence

The estimated average concentration of mercury for the earth's crust is about 0.5 ppm (Weast, 1968). Sedimentary rocks contain 0.04 to 0.4 ppm of mercury while mercury content in igneous rocks averages 0.08 ppm (Turekian and Wedephol, 1961). Joint FAO/WHO Expert Committee on Food Additives (1972) quotes the major source of mercury as the natural degassing of earth's crust and reports figures in the range of 25,000 - 150,000 tonnes of mercury per year. These figures are based on the work done by Weiss et al. (1971) on concentration of mercury in Greenland ice that was deposited prior to 1900. Korringa and Hagel (1974) have calculated the annual amount of mercury reaching the earth's surface due to precipitation of rainfall and arrived at a figure of approximately 30,000 tonnes. It is probably thought that the sources of this atmospheric mercury are volcanic gases and evaporation from oceans. These workers have also calculated the run-off of mercury from rivers having a natural background mercury level of 200 ng/l and this would account for approximately 5,000 tonnes per year.

Mercury concentration is expected in water bodies located near mercury ore deposits. This mercury reaches into the water

bodies by way of leaching and erosion of geological formations. Such waters are known to have mercury concentrations exceeding 5 ppb to 136 ppb (Kvashnevskaya and Shablovskaya, 1963) as against the reported natural background mercury level of 0.1 ppb of unpolluted rivers in areas where mercury deposits are not known (Dall'Aglia, 1968 and Heide, Lere and Bohm, 1957).

ii. Industrial Production

World production of mercury averaged about 4,000 tonnes per year over the period 1900-1940 (Korringa and Hagel, 1974). Mercury production in 1968 and 1969 were 9,836 and 10,885 tonnes, respectively (USDI Bur. of Mines, 1969). The average rate of increase of mercury production has been 2 percent per year. It is difficult to estimate the amount of mercury released into the environment as a result of mining and smelting of this metal. High levels of mercury in lake and stream waters have been attributed to the dumping of materials (Wallace et al., 1971). Losses through stack during smelting operations is expected within 2-3 percent. Therefore, losses to the atmosphere is expected to be of the order of 300-400 tonnes per year for 1970-75 productions. Korringa and Hagel (1974) take a very pessimistic point of view and conclude that there is every reason to assume that by about 1975 all the 11,000 tonnes of mercury produced per year due to mining operations will find its way into the environment.

iii. Uses of Mercury

Mercury is being used in several manufacturing processes in various industries. It is being extensively used in

electrical industries to manufacture batteries, high intensity street lamps, silent switches, fluorescent lights, etc. The biggest consumer of mercury are the chlor-alkali industries and it is perhaps the most serious polluter of our environment, particularly the aquatic environment. Mercury compounds are also used as catalysts in the manufacture of vinyl chloride, uretham plastics and acetaldehyde. The use of mercury has been increasing steadily in paint and pulp and paper industries. Mercurial fungicides are used for seed-dressing of agricultural products. Average consumption patterns for industrialised countries have been summarised by Korringa and Hagel (1974) as follows: chlor-alkali plants, 25 percent; electrical equipments, 20 percent; paints, 15 percent; measurements and control systems, 10 percent; agriculture, 5 percent; dental, 3 percent; laboratory, 2 percent and other uses including military uses as detonaters, 20 percent. The pattern of consumption in industrialised countries is similar to that published by D'Itri (1972) for the consumption of mercury in the U.S.A. in 1968. Recent concern over the environmental problems related to the use of mercury, has stabilised production and the discharge through waste has been reduced.

iv. Fossil Fuels

Since the beginning of the industrial revolution fossil fuels have been the main source of energy. Use of petroleum and coal has been increasing spirally since then. In 1968, the world-wide consumption of coal and oil was 3×10^9 and 2×10^9

tonnes per year, respectively. D'Itri (1973) has reported an average figure of 1,000 ppb of mercury concentration for coals of all types and 40 ppb for crude oil. On the basis of 1968 consumption of coal and oil, the total mercury released to the environment averages 3,000 tonnes per year. Heindryckx et al. (1974) calculated the amount of mercury released to the environment and gave the following figures: combustion of coal and lignite, 3,000 tonnes per year; refining and combustion of petroleum and natural gas, 400 tonnes per year; production of steel, cement and phosphate, 500 tonnes per year. Korrinda and Hagel (1974) made similar calculations and estimated for the year 1970, an annual release of 3,000 tonnes of mercury from coal burning, 1,250 tonnes from mineral oil and 250 tonnes from natural gas consumption. It was expected that a total of 5,000 tonnes of mercury would be emitted by 1975 from burning of fossil fuels. Smelting of sulfur ores is expected to contribute about 2,000 tonnes of mercury annually and making of cement and phosphate and other heating processes another 5,000 tonnes per year by 1975.

v. Sewage Disposal

D'Itri (1972) points out that sewage disposal might be an important source of mercury in the aquatic environment. It is stated that somewhere between 200-400 kg of mercury per million population may be released from sewage disposal units. This would amount to approximately 40-80 tonnes per year for the entire population of the U.S.A. It is further pointed out that

sewage sludge can retain high amounts of mercury (6-20 mg/kg). This sludge is sometimes used as a fertilizer resulting in widespread disposal of mercury or is sometimes heated in multiple hearth furnaces when most of the mercury would probably be released into the atmosphere. If the United States production is taken as being roughly 30 percent of world consumption, one might extrapolate the sewage release figure for the United States to indicate that something of the order of 1,000 tonnes of mercury may be released from sewage system on a global scale.

Considering the pessimistic view of Korringa and Hagel (1974), the total global release of mercury is taken as the sum of the global production plus the release from fossil fuels and natural gas and release from non-mercury related industries. It was calculated by these workers that by 1975 the total anthropogenic release of mercury on a global scale would be about 20,000 tonnes per year and about 30,000 tonnes would be as minimum release per year from natural sources, makes it 50,000 tonnes per year from all the sources.

b. Transport, Distribution and Transformation

Jenson and Jernelev (1972) have suggested different types of cycle for the distribution of mercury. One cycle is global in scope and depends upon the atmospheric circulation of elemental mercury vapours and most of the mercury is derived from natural sources. The other cycle is local and is predominantly concerned with man-made release.

i. Global Mercury Cycle

According to the estimates of Korringa and Hagel (1974) the minimum transport of mercury from the atmosphere to the earth should have been about 30,000 tonnes annually, prior to 1900. They also calculated the contribution of man-made release of mercury to the atmospheric transport cycle as 16,000 tonnes per year. It is assumed that out of this 46,000 tonnes of mercury, 41,000 tonnes per year would eventually find its way into the ocean. Korringa and Hagel (1974) also estimated the amount of mercury transported by rivers to the oceans to be 5,000 tonnes per year based on quoted figures of $37,000 \text{ km}^3$ of water flow via the rivers and a natural mercury content of less than $0.2 \mu\text{g/l}$ in river water. Heindryckx et al. (1974) assume that 50,000 tonnes of mercury are released each year to the atmosphere and a major part of this is returned to the oceans via precipitation. With these assumptions, Heindryckx et al. (1974) concluded that the background level of mercury in air would lie between $1\text{--}10 \text{ ng/m}^3$. An important conclusion that has been drawn from these calculations is that the concentration of mercury in the oceans should not change substantially in the foreseeable future. The movement of mercury among the atmosphere, soil and water components of the environment is depicted in Fig. 1.

ii. Local Mercury Cycle

Both the inorganic and organic forms of mercury discharged into the aquatic environment are subject to the

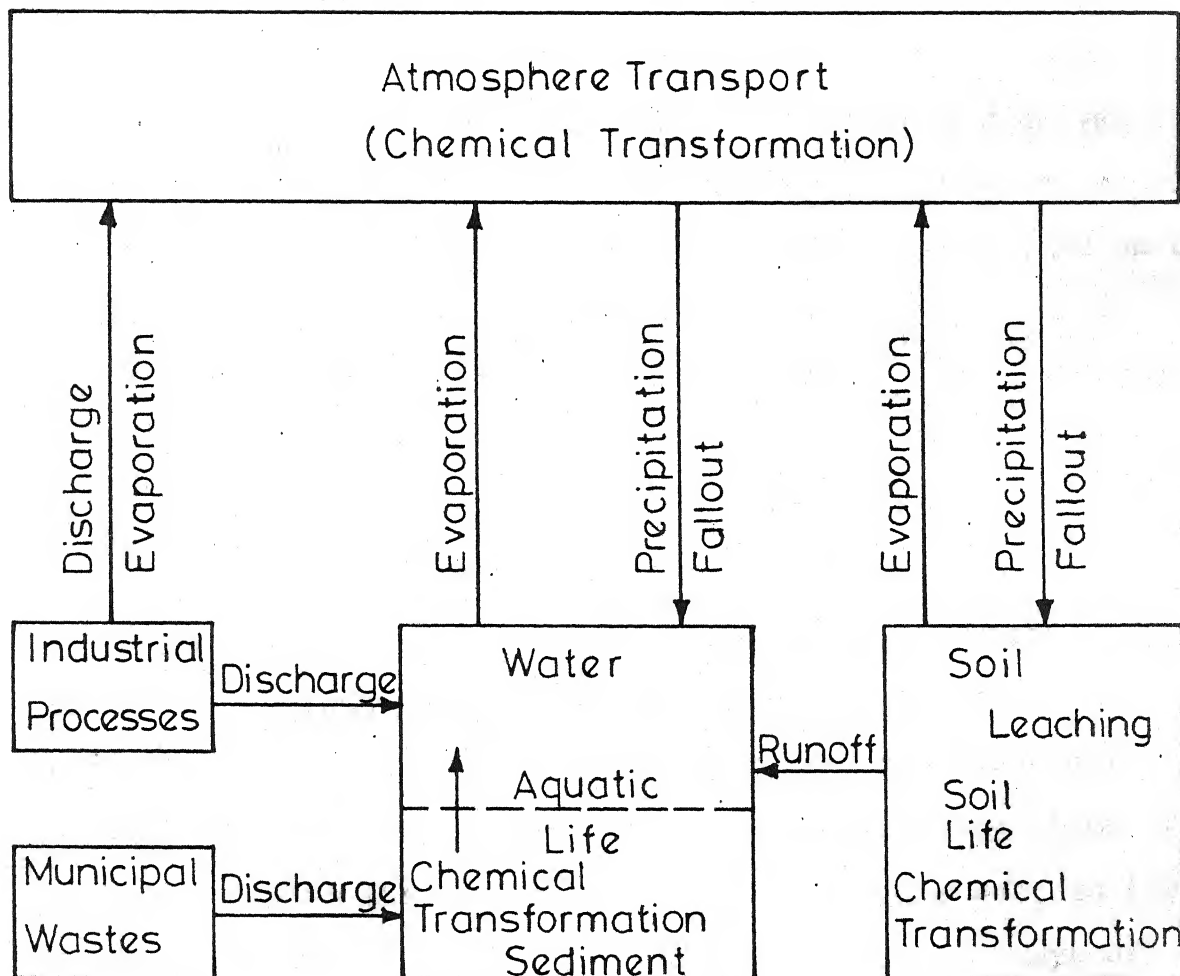


Fig. 1 -Mercury Cycle in the Environment.

conversion. The inorganic forms of mercury (Hg^0 and HgS) undergo transformation mainly by oxidation-reduction reaction (Jensen and Jernelov, 1972) and is greatly favoured in presence of organic substances. Ionic mercury is capable of forming a wide variety of complexes and chelates with organic materials. Under anaerobic conditions, highly soluble mercury (II) sulfide is formed owing to the presence of hydrogen sulfide gas.

Divalent inorganic mercury (II) can undergo two important reactions. The first is the reduction to metallic mercury under reducing conditions. Divalent mercury can also be converted to metallic mercury by certain bacteria, particularly of the genus Pseudomonas (Magos et al., 1964). The second important reaction that ionic divalent mercury (Hg^{++}) undergoes in nature is its conversion to methylmercury and dimethylmercury compounds. It has been sufficiently demonstrated that biological methylation of mercury occurs in the sediments of river and lake bottoms (Jensen and Jernelov, 1969). There are two biochemical pathways of mercury methylation, one anaerobic and the other aerobic. The anaerobic pathway involves the methylation of inorganic mercury by methyl cobalamine compounds produced by methanogenic bacteria under mildly reducing conditions (Wood et al., 1968). The process is non-enzymic and strictly anaerobic. Despite the fact that anaerobic pathway for methylmercury production is well-known, it seems unlikely that significant amounts of methylmercury are formed in the aquatic environment under anaerobic conditions. The chief reason for this as pointed out by Jensen and Jernelov (1972) is

that in natural water when oxygen is exhausted, hydrogen sulfide is formed and divalent mercury becomes bound as mercury (II) sulfide. In this sulfide form mercury is not available for methylation under anaerobic conditions.

The aerobic pathway has been described by Lander (1971) in studies of Neurospora crassa. His findings indicate that methylmercury bound to homocysteine becomes methylated by those processes in the cell normally responsible for the formation of methionine. The cycle of mercury interconversion in nature is presented in Fig. 2.

c. Bioconcentration

Methylated forms of mercury are highly toxic than other forms of mercury as well as they are more biologically mobile. Methylmercury have a strong tendency to bioaccumulate and while it is very efficiently absorbed in biological membranes, its degradation and excretion is much more slow than other mercury compounds. It possesses a very high chemical affinity for the sulfhydryl group, which occurs mainly in proteins in living organisms. Once methylmercury has entered the organism, is soon converted to a non-diffusible protein-bound form.

The accumulation of methylmercury in food chains has been proposed as a three-step process (WHO, 1976). The first-step is the accumulation by bottom fauna that are in closest proximity of methylmercury formation. The accumulation in the bottom fauna including plankton, would be followed by accumulation in species such as roach and finally in the large carnivorous fish.

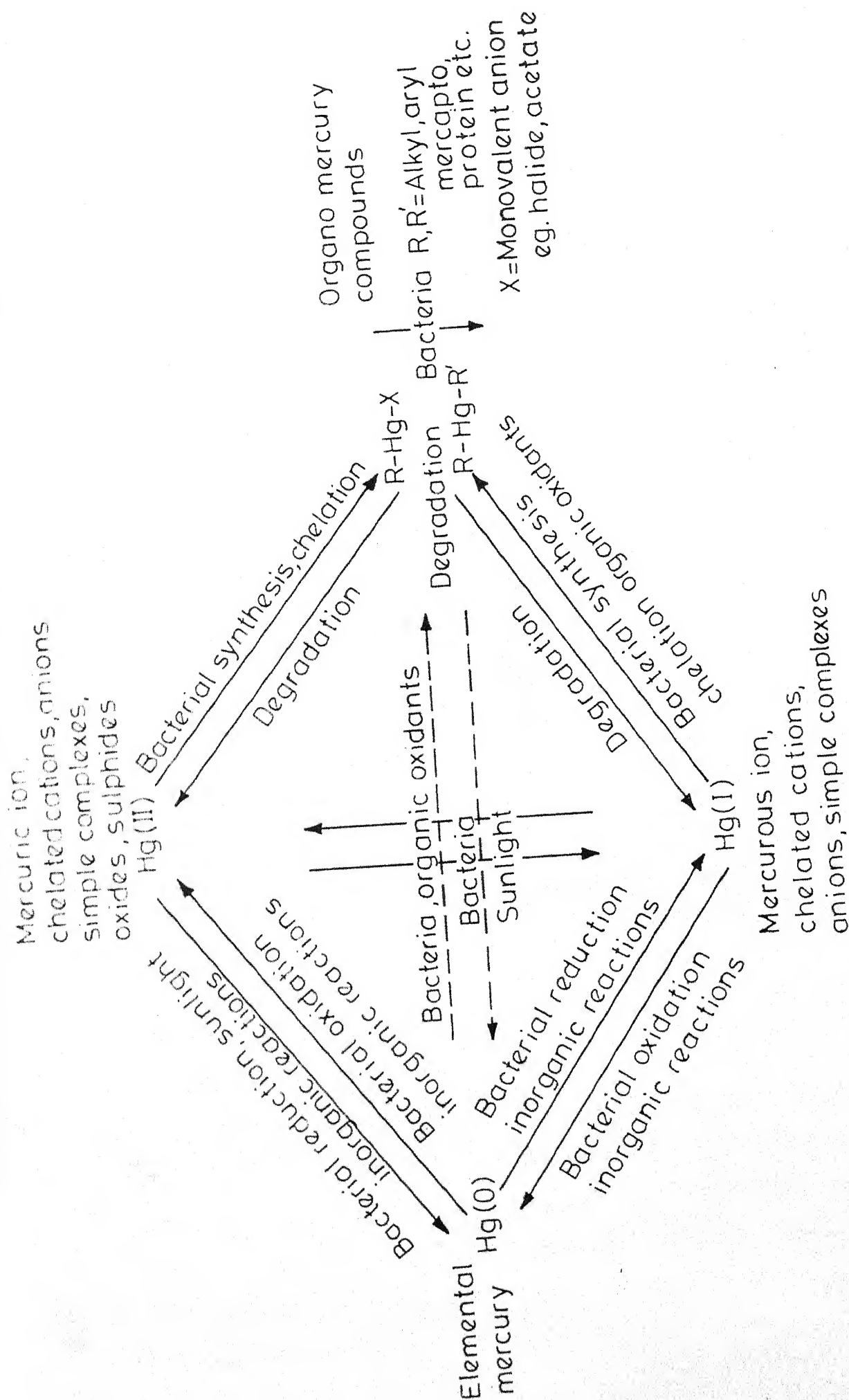


Fig. 2 - The Cycle of Mercury Interconversion in Nature.
(Adapted from D'Itri, 1973)

Accumulation of mercury in the terrestrial and aquatic food chains results in risks for man mainly through the consumption of: game birds in areas where methylmercury fungicides are in use; fish from contaminated waters; other sea foods; and fish-eating birds.

d. Environmental Levels of Mercury

The levels of mercury in the environment have been reviewed by several workers and agencies (Holden, 1972; D'Itri, 1972; Joint FAO/WHO Expert Committee on Food Additives, 1972). Their principal findings are as follows. The concentration of mercury vapour in the atmosphere is so low that it does not contribute significantly to human intake of mercury excepting few 'hot spots' that may exist. Concentration of mercury in water, particularly drinking water are also low to contribute significantly to human exposures. The industrial release of different forms of mercury into land waters has led to local pollution, which may result in an increase of mercury in fish and transferred subsequently to man.

i. Air

The average concentration of mercury in general atmosphere is reported to be 20 ng/m^3 (Saha, 1972). Goldwater (1971) reported the background level of mercury in the atmosphere under normal conditions to be less than 1 ppb. Williston (1968) reported mercury levels in the vicinity of San Francisco, U.S.A. to be $0.5\text{-}50 \text{ ng/m}^3$ and noted a correlation between increased mercury content and smogs caused by thermal inversion. Fugimura (1964) reported air levels upto $10,000 \text{ ng/m}^3$ near rice fields

where mercury fungicides had been used and values upto 18,000 ng/m³ near a super highway in Japan. McCarthy et al. (1970) noted air values upto 600 and 1,500 ng/m³ near mercury mines and refineries respectively.

ii. Water

Data for concentration of mercury in rainwater and snow are limited. Brune (1969) noted values of approximately 300 ng/l in rainwater in Sweden. Analysis of ice deposited in Greenland prior to the 1900s (Weiss et al., 1971) indicates values of 60 ng/kg.

Some of the high mercury levels reported in the surface waters in various parts of the world are shown in Table 1. Natural mercury contents of unpolluted rivers in areas where mercury deposits are not expected are less than 0.1 ppb (Dall'Aglia, 1968). Voegelé (1971) reported levels upto 40 ng/l for uncontaminated Canadian waters. Durum et al. (1971) have reported concentration of mercury in surface waters in U.S.A. upto 200 ng/l in areas where mercury mineralization was present. Dall'Aglia (1968) measured mercury concentrations as high as 136 ppb in Italian rivers which drained basins having worked and unworked mercury deposits.

In ocean water the reported values fall between 0.03-3 ppb (Ardinian et al., 1963; Brune, 1969; Mason, 1966). Hosohara (1961) reported that the total mercury content of waters of Minamata Bay, Japan ranged between 1.6-3.6 ppb and 3.5 to 19 ppm in plankton suggesting that considerable amounts of mercury in the water are consumed or absorbed by plankton.

Table 1
Mercury Levels in Natural Waters

Source and Location	Average Mercury ppb
Pascagoula river at Merrill, Miss	3.00
Missouri river near St. Louis, Mo	2.8
Maumee river at Antwerp, Ohio	6.00
Wisconsin river near Nekoosawis	2.4
Volga, Don, Araks and Danube rivers	1-2
Rivers near mercury deposits of Italy	upto 136
Minamata Bay, Japan	1.6 to 3.6
Ganga river, Kanpur, India	0.3

Source: 1. Mercury in the Environment. Geological Survey Prof. Paper 713 (1970).

2. Dutta, A., Unpublished M.Sc. Project Report. Deptt. of Chemistry, IIT Kanpur, (1978).

iii. Food--

Milk, meat, meat-products, egg, fish and various kinds of cereals are the susceptible items of mercury poisoning. Smart (1968) has reviewed data concerning mercury concentrations in foods. Mercury levels in milk in Germany and United Kingdom has median value of 6 $\mu\text{g/kg}$. Levels in eggs from Denmark, Germany and United Kingdom ranged between 10-20 $\mu\text{g/kg}$. In meat and meat-products the concentration varied between 10-20 $\mu\text{g/kg}$ whereas levels in cereals from same countries ranged upto 50 $\mu\text{g/kg}$.

The WHO Regional Office for Europe (1973) has reported that fish from contaminated fresh water areas may have values of 200-5,000 $\mu\text{g/kg}$ and from heavily polluted waters, values may be as high as 20,000 $\mu\text{g/kg}$. In India, the reported level of mercury in few samples of fish from the Bombay coast was 500 ng/g (Tejam and Haldar, 1975). Mercury in fish appears to be predominantly in the form of methylmercury.

e. Toxicity and Biological Effects of Mercury

Uptake of mercury can be by inhalation, ingestion, absorption through skin and it is excreted through urine, feces and milk. The mercury gets distributed in different organs and systems of the body. Cell membrane is the first site of attack as it contains sulfhydryl groups which are known to have a very high affinity for mercury compounds (Ruthstein, 1973). Almost all proteins contain sulfhydryl groups and thus every protein in the body is a potential target. Depending upon the level and duration of exposure, the damage may be reversible or irreversible.

The signs and symptoms of acute toxicity are severe gastrointestinal damage, shock, cardiovascular collapse, renal failure in case of large doses of divalent mercury and pulmonary irritation when the vapours are inhaled. These reflect the fact that all mercury compounds are chemically reactive, can denature proteins, inactivate enzymes and disrupt cell membranes. Methyl and ethylmercury compounds are neurotoxic and lead to destruction of neurological cells in cortex, particularly in the visual areas and may lead to complete blindness (Hunter et al., 1954).

Occurrence of mercury in mammary glands would confirm presence of mercury in mother's milk (Berlin and Ullberg, 1963). Methylmercury crosses the placental 'barrier' and achieves 30 percent higher concentration in fetal red blood cells than in maternal red blood cells. Studies on the genetic effects of organomercurials have reflected effects such as on mechanism of cell division (c-mitosis), chromosome breakage and gene mutation. Experiments with fruit flies have shown that organomercurials affect the mitotic spindle of the cells in such a way that the number of chromosomes is doubled or individual chromosomes are defectively distributed during mitosis (Ramel, 1967).

f. Behaviour of Mercury in Aqueous Media

Under the usual conditions of temperature that occur in river and lake water and water-saturated sediments, mercury can be present in one or more of the three different oxidation states. The most reduced, in a chemical sense, of these forms is the mercury metal, which is a liquid at ordinary temperature. The

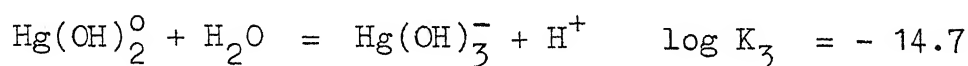
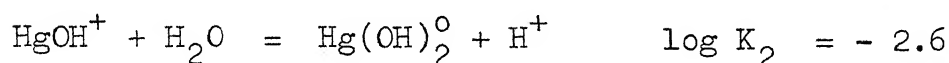
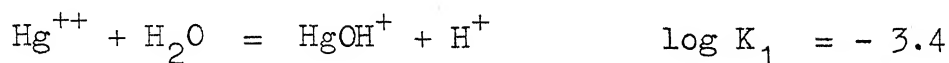
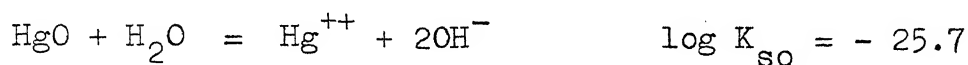
other two forms are ionic; the more reduced of the two ions is the mercurous ion (Hg_2^{++}). In oxidising conditions, especially at low pH, the stable form is the mercury (II) ion (Hg^{++}).

Mercury (II) is well-known for its ability to form stable complexes with inorganic ligands. Although bonding through oxygen is weaker than - S (sulfur) or - N (nitrogen), it is strongly hydrolysed compared to most divalent metal ions. A set of data for the hydrolysis is chosen from Sillen and Martell (1964) and is shown in Table 2. The maximum concentration of $\text{Hg}(\text{OH})_2^0$ is much higher than the solubility of most divalent heavy metal hydroxides. Mercury (II) forms strong complexes with halides in the order of $\text{Cl}^- > \text{Br}^- > \text{I}^-$. The stability constants for chloro complexes are also shown in Table 2. In solutions of mercury (II) and chloride ions where the molar ratio of chloride to mercury is two, the only species occurring will be Hg^{++} , HgCl^+ , HgCl_2 and $\text{Hg}(\text{OH})_2$ (Marcus, 1965). When there is an excess of free chloride ion the complexes HgCl_3^- and HgCl_4^{--} are formed in addition to the above species. Above one molar concentration of chloride ion, only HgCl_4^{--} is present (Marcus and Elizer, 1965). This chloride interference decreases at higher pH as Cl^- is replaced by OH^- (Friedman and Masari, 1973). All of these forms of ionic mercury exist in equilibrium with each other. HgCl^+ and HgCl^- are probably the less prevalent species.

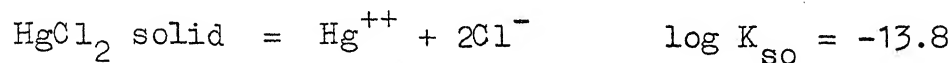
Inorganic ligands found in natural waters with strong affinities for Hg^{++} ion seem to be numerous. It is interesting to note that metal ions normally found in natural waters are associated

Table 2
Stability Constants for Mercury Species

Hydrolysis Data



Chloride Complexes



Model Parameters

$$r \text{ Hg}^{++} = 1.1 \text{ \AA}, \quad r \text{ H}_2\text{O} = 1.3 \text{ \AA}$$

$$\text{Area per Hg(II) complex} = 50 \text{ \AA}^2$$

$$\text{Ionic strength } 10^{-1} \text{ mole dm}^{-3}$$

with the hydrous oxide, clays and biological organic matter. Apparently, mercury discharged into receiving waters may be transformed chemically, physically and/or biologically under appropriate conditions, undergo sorption and/or surface complexation on inorganic or organic sorbents and subsequently adsorbed or ingested by living organisms.

g. Mercury Measurement

Several reviews have appeared recently concerning methods of mercury determination (D'Itri, 1972; NIOSH, 1973 and Burrows, 1975). The most frequently used methods of measurement of total mercury are colourimetric (dithizone), flameless atomic absorption and neutron activation. The flameless atomic absorption method has become the 'work horse' for measurement of mercury in environmental samples. Instruments based on flameless atomic absorption are available specifically for mercury measurement.

Determination of mercury by colourimetric measurement of a mercury-dithizone complex has been the basis of most of the methods till 1960s. Other related methods using dithizone for measuring mercury in environmental samples have been described by Smart et al. (1969) and Elly (1973). The above procedures make use of the wet oxidation of the sample followed by extraction of mercury in an organic solvent as a mercury-dithizone complex and finally the colourimetric measurement of the complex itself. The dithizone procedure has a sensitivity of 2 µg/l of mercury for water analysis.

The latest developments in atomic absorption procedures have been recently reviewed by Burrows (1975). Winterland and Clements

(1972) have described a procedure that will measure mercury in water in the range of 200 ng/l without preconcentration. Measurement of very low levels of mercury in water samples requires some preconcentration. The technique of atomic absorption procedure is simple and sensitive and have detection limit in the range of 0.5 to 5 ng of mercury.

Procedures for neutron activation analysis of total mercury have been described by Westermarck and Lunggren (1972) and Burrows (1975). The method is based on the principle that when natural mercury is exposed to high flux of thermal neutrons, it is converted to a mixture of radio isotopes. After the sample has been irradiated with neutrons, a precise weight of carrier mercury is added and then subjected to digestion and organic destruction. On completion of digestion, mercury is isolated by electrodeposition and the radioactivity is determined by a gamma counter. The limit of detection is 0.1-0.3 ng of mercury.

Considering the present methods for the determination of total mercury in environmental samples, it would appear that the method of choice is that of flameless atomic absorption. Neutron activation is principally of use as a reference method.

B. Coal

1. Chemistry of Coal

Coal may be defined as a compact stratified mass of mummified plants which have been modified chemically in varying degree, interspersed with smaller amount of inorganic matter

(Francis, 1950). The greater the proportion of carbon content, higher the rank and further the coal has departed from the composition of original plant debris. Increase in rank denotes the natural process whereby the carbon content is increased at the cost of hydrogen and oxygen content.

As can be seen from Table 3, the H/C ratio is fairly low during practically the whole coalification process, indicating a rather high aromatic content. Considering that graphite is the final link in the coal evolution, it is a logical conclusion that the aromaticity and the degree of condensation of the aromatic rings increase throughout the sequence. The reaction processes coal may undergo can be distinguished into three categories:

1. Reaction processes leaving the coal molecules as such intact including the reactions of the peripheral functional groups and solvolysis.
2. Reaction processes converting the coal molecule as gently as possible into identifiable products of lower molecular weight--hydrogenolysis.
3. Reaction processes causing a drastic destruction of coal molecule including oxidation, carbonization or thermal cracking.

2. Surface Chemistry of Coal

Graphite is the ultimate evolved form of coal and can be considered as the basic structural unit. This structure is composed of a system of infinite layers of fused hexagons with carbon-carbon bond distance of 1.415 \AA within each layer. Three

Table 3

Functional Group Analysis of Coal (in weight percent)

	C	H	N	S	O _{tot}	O _{COOH}	O _{OCH₃}	O _{OH}	O _{C=O}	Summed up
										0
Peat	60.0	4.9	0.9	0.05	33.9	5.1	0.9	12.3	11.6	29.9
Brown coal	65.5	5.1	0.9	0.2	27.8	8.0	1.1	7.2	6.5	22.7
Lignites	69.6	4.6	0.3	3.1	21.9	3.9	-	12.5	7.2	23.6
	71.7	4.9	0.8	0.4	22.6	5.1	0.4	7.8	9.3	22.6
	75.9	5.3	1.6	1.1	16.2	1.6	0.3	7.5	7.4	16.8
Hard coals	79.5	5.5	3.2	0.8	11.1	0.3	-	6.1	4.9	11.3
	80.2	4.9	1.2	0.6	13.4	1.0	-	8.3	3.1	12.4
	85.5	5.3	0.6	0.5	7.9	-	-	5.6	1.6	7.2
	87.0	5.3	1.9	0.7	5.1	-	-	3.1	1.7	4.8
	88.6	5.0	2.3	0.8	3.0	-	-	1.9	1.8	3.7
	90.3	4.7	1.7	1.0	2.9	-	-	0.5	2.0	2.5
	90.9	4.1	1.7	0.9	2.0	-	-	0.6	1.9	2.5

Adapted from Blom (1960).

of carbon's four electrons are engaged in forming regular covalent bonds with neighbouring atoms and are localised while the fourth resonates between several valency-bond character, giving each carbon-carbon bond a one-third double bond character. Parallel graphite planes are held apart by approximately 3.35 \AA by relatively weak van der Waals forces. The carbon atoms are directly superimposed in alternate layers, the configuration being confirmed by X-ray diffraction spectra (Walker, 1962).

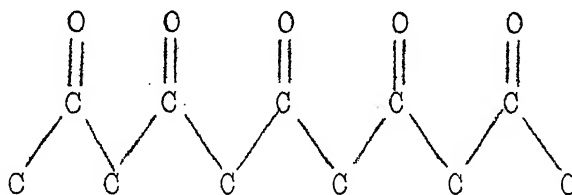
In carbons, the fraction which exists in the form of disordered, single, unstacked graphite like layers susceptible to chemisorption while the fraction shows some degree of well ordered parallel stacking is less susceptible. The disordered fraction is higher in microcrystalline carbons than in crystalline carbons. There are many exposed defects, dislocations and discontinuities in the layer planes of the microcrystalline carbons apart from the edges of the carbon layers, such sites called active sites, are associated with high concentrations of unpaired electron spin centre and therefore expected to play a significant role in chemisorption. Surface carbon atoms located at active sites due to residual valencies, show a strong tendency to chemisorb other elements like oxygen, hydrogen, nitrogen, chlorine, bromine, iodine and sulfur and give rise to non-stoichiometric stable surface compounds called surface complexes. Many of the surface reactions arise either because of their tendency to chemisorb other elements or because of a superficial layer of chemically bonded elements (Puri, 1970).

Oxygen is chemisorbed more readily than any other elements and hence carbon-oxygen complexes are by far the most important in influencing surface reactions, surface behaviour, wettability, electrical and catalytical properties of carbons. Oxygen combines with carbon directly to form physicochemical complexes C_xO_y of variable composition, giving a mixture of CO_2 and CO . It is now known that almost all types of carbons are covered with oxygen complexes. These complexes are often the source of property by which carbon becomes useful or effective in certain respects.

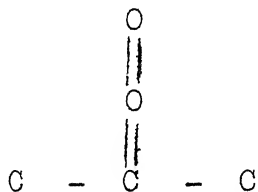
Puri (1970) suggested several hypothetical structures and formulas assigned to carbon-oxygen complexes as shown:

Oxygen layer
at the surface

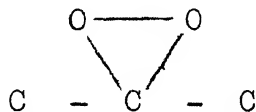
Body of the
filament



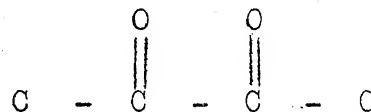
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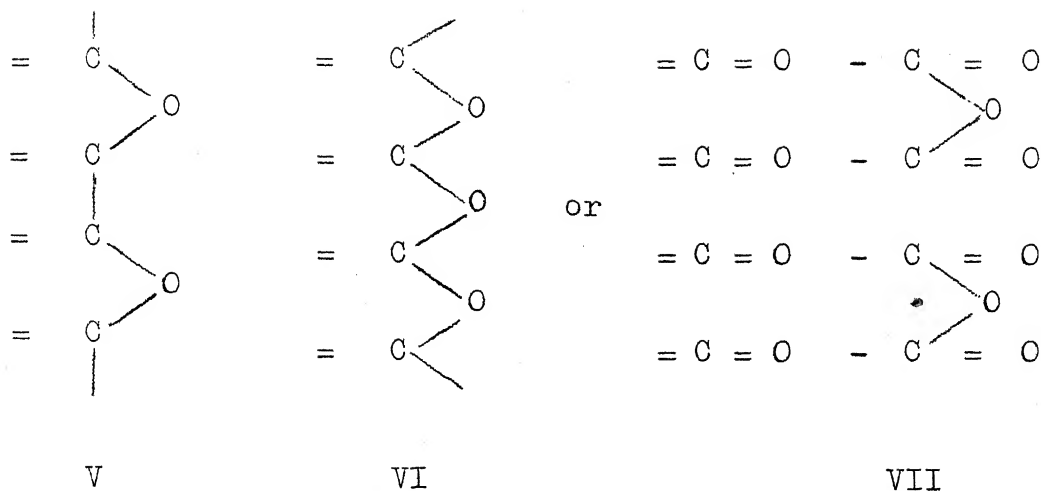
II



III



IV



The primary step in combustion is dissociative sorption of oxygen to form oxygen complexes. Below 500°C, the rate of formation of these complexes exceeds their rate of decomposition, but at higher temperature, the complexes become less stable and the rate of their decomposition into CO₂ and CO exceeds the rate of their formation. Formation of CO₂ and CO requires appreciable concentration of oxygen complexes.

Whatever be the exact nature of surface oxides, the combined oxygen is present mainly at the edges of giant molecules that constitute the main sorbing surface, the oxygen complexes exercise a considerable influence on the surface behaviour and surface reactions of carbons. Presence of carbon-oxygen complexes reduce hydrophobicity of carbons and imparts polar character to them exercising preferential sorption.

Hydrogen is invariably present in all coals and most carbons, as these are **pyrolysed** residues of organic compounds. The hydrogen is present as chemisorbed water and as hydroxyl,

hydroquinonic and carboxyl groups. Besides these forms, hydrogen is present in direct combination with carbon atom. It is held even more firmly than oxygen. The hydrogen content is about 5 percent as compared to oxygen content varying between 2 to 30 percent. Because of low atomic weight, the hydrogen content is very important. Hydrogen may bind one mobile electron. The aromatic/aliphatic ratio increases markedly with the carbon content (Stacy, 1966). The aromatic hydrogen is considered to be covalently bonded to the carbon atoms at the periphery. The aliphatic hydrogen is present in the form of aliphatic chains attached to the periphery of aromatic rings. A part of the hydrogen is present at the surface and the rest of it is dispersed in more than one layer in the interior of the particles.

Nitrogen is present in coal and carbons though the quantities are not significant. Affinity of nitrogen is indicated by increase in nitrogen content with the carbon content. Fixation of nitrogen by carbons depends upon nature of oxygen containing groups initially present on the surface. Presence of nicotinic acid has provided unequivocal evidence of the presence of a nitrogen heterocyclic ring system in coal. About 45 percent of the nitrogen is present in amine structures. As nitrogen is present in ring structure, it implies that the nitrogen containing ring becomes partially opened during hydrolysis, yielding amines (Van Krevelen, 1961).

Sulfur, like oxygen, hydrogen and nitrogen is almost invariably present in coals in inorganic or organic forms. Organic

sulfur compounds are distributed uniformly throughout the coal as part of its fundamental constitution. The fraction which is present as free sulfur or in combination with metals is known as inorganic sulfur. The binding of sulfur is similar to that of oxygen. The sulfur present in carbon is fixed as C-S-C or C-S-S-C groups. The fixation takes partly by substitution of quinonic and phenolic groups and partially by addition at the unsaturated sites. The C-S complex is highly stable. The carbon-sulfur complexes may lead to the formation of peripheral heterocyclic structures on the layer lattices in the carbon surface or to sulfur bridges between the adjacent layers. The distribution of sulfur in inorganic and organic forms depends on the metal and hydrogen contents of the coal. The inorganic form of sulfur gets oxidized to sulfates. Organic sulfur, apart from carbon-sulfur complexes can exist as - C - SH, CH - SH and CH - S - CH depending upon the hydrogen available.

Functional groups formed by oxidation makes the carbon hydrophilic. The most common groups positively identified on the carbon surface are carboxyl, hydroxyl, phenolic and carboxyl. Other possible groups include lactones - a condensation product of the adjacent carbonyl and carboxyl groups, quinoid structures from oxidation of adjacent phenolic hydroxyls and hydroperoxides. The quantitative estimation of functional groups on oxidized cold milled graphites is given in Table 4 (McKee and Mimeault, 1973).

Table 4

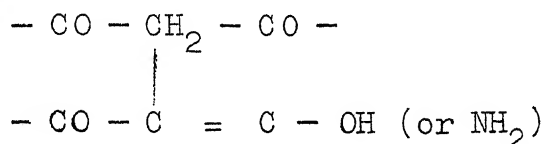
Functional Groups on Cold Milled Graphites

Groups	Amount, meq/m ²
$\begin{array}{c} \text{O} \\ \\ - \text{C} - \text{OH} \end{array}$	0.48
$\begin{array}{c} \nearrow \text{C} - \text{OH} \end{array}$	0.16
$\begin{array}{c} \nearrow \text{C} - \text{OOH} \end{array}$	0.04
$\begin{array}{c} \nearrow \text{C} = \text{O} \end{array}$	0.07

Identification of surface functional groups with the help of IR spectra has peaks at 3450, 3030, 2920, 1600, 1450, 1380, 1260, 1025, 870, 820 and 750 cm⁻¹ (Burvas et al., 1970). The major difference between the IR spectra of coals and lignites is that the latter shows no absorption around 3030 cm⁻¹ by the vibration of C-H groups. A characteristic of low rank coals, peats and relative humic materials is that much of the oxygen associated with their structure is present as carboxyl groups imparting ion-exchange properties (Schafer, 1970). Shih et al. (1972) attributed the absorption band at 1600 cm⁻¹ to the presence of aromatic structures and concluded that the contribution of aromatic structure increased with the rank or the temperature to which it is heated. Hydrogen

bonding by protons with oxygen groups is one of the surface interactions (Mattson et al., 1969; Mattson and Mark, 1969 and Mattson et al., 1970). Edges of microcrystallite planes and amount and distribution of ash content contribute substantially to the active sites for sorbates (Soneyink and Weber, 1967).

Oza (1974) used IR spectra in characterizing three Indian coals, viz., Neyveli, Churcha and Giridih. All coals revealed intramolecular bonded OH groups at bands 2350 cm^{-1} . Churcha and Giridih coals showed bands at 1600 cm^{-1} representing the



groups. Bands at 1350 cm^{-1} on Churcha and Giridih coals may possibly be due to $-\text{N}-\text{CS}-\text{N}-$ thioesters. The bands at 1100 cm^{-1} appearing on all coals may be representing C-H in plane deformation and benzene ring substitution. Absence of bands at 1400 cm^{-1} on Neyveli coal indicates relative absence of alkanes and aromatic hydrocarbons which are present on Churcha and Giridih coals. This may be interpreted as relative absence of volatile matter in Neyveli coal as against predominance of volatiles on Churcha and Giridih coals.

C. Use of Coal in Water and Wastewater Treatment

Use of coal in water and wastewater treatment is not a new proposal. In the United States anthracite coals have long been used in water treatment as filter media. A notable use of coal

for industrial waste treatment is reported by Gutzeit and Enyart (1962). They used bituminous coal as sorbent for oils and hydrocarbons. An investigation into the use of coal for tertiary treatment of domestic wastewater was conducted by Johnson et al. (1966). These workers studied various types of American coals and concluded high-volatile bituminous coals as most suitable. They also concluded that some coals were capable of removing organic materials and that the economics of coal based polishing treatment for secondary effluent compared favourably with the processes employing activated carbon. Carlton et al. (1965) investigated the suitability of coal for use in the treatment of sewage and observed that (i) all American coals above the rank of lignite were suitable for use as filter media, (ii) all coal studied demonstrated tendency to absorb dissolved organic matter, (iii) selected types of inorganic matter in solution could be removed from water by coal and (iv) no coal was observed to contribute chemical oxygen demand to the water. Shannon and Silveston (1968) studied the use of coal for the sorption of dissolved chemical oxygen demand of a synthetic wastewater and observed that unlike activated carbon, coal displayed selective adsorption for the components of synthetic wastewater. King et al. (1969) experimented on the use of coal as a sorbent for pesticides and phosphorous containing compounds waste and reported varying degrees of success. Manahan et al. (1975) concluded in their investigation that coal can be used to remove acid, iron and heavy metals from water and the exhausted coal could be regenerated. George and Chaudhuri (1977) demonstrated the suitability of bituminous coal in removing iron from ground water.

Due to lack of good quality anthracite supply in India, bituminous coals were evaluated as substitute for anthracite in dual-media filtration (Paramsivam, 1972). In a plant-scale study, Ranade (1976) was able to improve the filtration rate by converting a rapid sand filter to a dual-media coal-sand filter without any significant deterioration of the water quality. Oza and Chaudhuri (1976) reported sorption of virus onto bituminous coal and Sriramulu (1975) studied virus removal by filtration through coal with varying degrees of success.

D. Removal of Mercury from Water and Wastewater

Very little information is available on mercury removal by conventional water treatment processes. Gary et al. (1973) investigated the removal of inorganic and organic mercury by coagulation, filtration and water softening processes. Removal of mercury from waters of varying turbidity using alum and ferricsulfate as coagulant was studied. In the turbidity range of 10-100 JTU alum removed 10-60 percent of inorganic mercury while removal of methylmercury was less under similar conditions. Ferricsulfate removed 40-60 percent of mercury in the turbidity range of 2-100 JTU. In case of inorganic mercury, removals steadily increased and over 60 percent of mercury was removed when turbidity was 100 JTU. Methylmercury removal indicated similar trend. Mercury removal depended only slightly upon the initial mercury concentration. Increased coagulant dose did not achieve any significant increase in removal of mercury. Removal of mercury during filtration

through conventional sand media did not remove any appreciable quantity of mercury and it is reported that the capacity of sand to remove mercury is limited. In softening processes mercury removal was pH dependent and 30 percent removal was obtained at pH 9.4 while at pH 10.6-11.0, 60-80 percent removal of inorganic mercury was obtained. Removal of methylmercury was not significant in this pH range.

Many investigations on the sorption of mercury in soils, sediments and rocks have been conducted by geologists and agriculturists (Fleischer, 1970 and Jonason, 1970). Various sorbents which have been investigated are, sands, clays, organics, minerals, alloys, activated carbon, ion-exchangers, nylons, polyesters, polypropylene, agricultural products, wools, chicken feathers, milk proteins, hair etc. (Friedman et al., 1971; Reimers and Krankel, 1972; Feick, Johnson and Yeaple, 1972; Tratnyek, 1972; Friedman and Weiss, 1972; McKaveney et al., 1972 and Michelsen et al., 1975). All such sorbents for which informations were available have been compared by Reimers et al. (1974). The greatest uptake has been observed by the organic mercaptans, demonstrating the basic affinity of mercury for sulfur. The sulfides are next in adsorptive capacity, but when high sulfides occur, inorganic mercury forms the soluble mercuric disulfide complexes. The organic mercaptans, which do not form the charged complexes, have been observed to be better binding agents for inorganic mercury. Next to the sulfur containing sorbents, the best adsorbers of mercuric chloride are some of the synthetic scavengers, including silicon alloys, ion-exchange resins

and activated carbon. Competitive to these scavengers as a mercuric chloride binder are the protein scavengers, such as wools, chicken feathers and hair. The clays, Illite and Montmorillonite and reduced sands are found to be fairly strong in their binding capacity. Peat has the greatest affinity for mercury and compares very well in its capacity with other scavengers and sediments.

Robert and Rowland (1973) investigated the efficiency of chemically modified cotton celluloses in sorbing mercury (II) from aqueous solutions. Despite the numerous differences among the chemically modified cotton celluloses, their performance in removing mercury from dilute aqueous solutions was remarkably similar when sufficient quantities of the various compositions were employed to provide an equivalent numbers of amine groups. The modified cotton celluloses were most effective in removing mercury (II) as well as methylmercuric ions from aqueous solutions. Trantnyek (1972) reported 90-95 percent of organic and inorganic mercury removal in 24 hr by waste wool from 1 ppm initial concentration.

Michelsen (1975) used protein based materials like casein and lactalbumin, whey and hair (keratin) for mercury removal. Casein-containing materials were more effective in removing mercury (II) ion but less effective in removing methylmercuric ion. Casein and whey contain nearly the same percent of nitrogen; casein contains no free sulfhydryl groups while whey does contain sulfhydryl groups. The observed removal superiority of mercury (II) ion with casein is not explained and perhaps it is difficult to explain in terms of nitrogen and sulfur containing groups. One possible explanation

may be the presence of phosphorous in casein. The interaction of mercurials with phosphoryl groups is well documented in cell membranes in literature.

Michelsen et al. (1975) also modified the tire tread rubber and employed the same for mercury removal. They produced cationic and anionic exchangers from tire tread rubber and compared their performance with the Dowex resins. All rubber modifications proved to be superior with respect to mercury loading capacities. They observed that at low concentrations, removal of mercury was first order reversible reaction process with respect to mercury concentration. These workers also demonstrated the feasibility of using hair in mercury removal and suggested the possibility of using a moving or fluidised bed. The spent hair could be regenerated like any other ion-exchange resin without much loss in capacity.

A number of commercially feasible techniques have been developed for removing ionic mercury from waste streams. Ion-exchange methods have been developed based on the use of cationic and anionic exchange resins (Gardiner and Frank, 1971 and Rosenzweig, 1971). Other techniques include the reaction of ionic mercury with sodium sulfide or hydrogen sulfide and precipitation with a flocculent; the reduction of ionic mercury to metallic mercury with an aldehyde followed by centrifugation; the decomposition of organomercurials with sulfuric acid and subsequent precipitation as mercuric sulfide and the use of sulfide-containing activated sludge to trap ionic mercury. Chlor-alkali industries use several processes for treatment of mercury-containing waste. One is

precipitation with sodium hydrosulfide followed by settling and activated carbon treatment (Litton System, Inc., 1971).

The literature is in agreement that commercial activated carbon is effective in removing mercury ions. Wehman (1972) worked with activated carbon-mercury systems and found reasonable removals and concluded that chelation of mercury improved activated carbon removal capacity. The vinyl chloride industry has long utilised carbon as a matrix for the mercuric chloride catalyst required in the conversion of acetylene to vinyl chloride. The catalyst is prepared by adsorption of mercuric chloride solutions. Sigworth and Smith (1972) investigated adsorption of inorganic compounds and found that most of the metals including mercury had high adsorption affinity for activated carbon. Mercury ion is reduced on carbon surface to the metal form and gets adsorbed on activated carbon. Methylmercury is also readily adsorbed. Smith et al. (1971) conducted carbon adsorption experiments with 13 mm dia column and a bed depth of 30 cm. They did not report any major problem and concluded that experimental equipment was adequate for testing carbon adsorption of mercury. It was hypothesised by these investigators that reduction of mercury (II) to the elemental state may proceed subsequent to adsorption. If this occurs, one might expect the thermal regeneration of activated carbon and recovery of mercury would be feasible.

Oppald (1971) observed that effluent mercury concentrations from a precipitation-adsorption-filtration process could be reduced from 30-100 ppb to 3-5 ppb by lowering the pH from neutral

to four. Wehman (1972) observed that activated carbon capacity steadily increased when the pH was lowered from nine to two.

The literature also indicates that sulfurizing agents such as carbon disulfide could be used to improve mercury removals. Suggs et al. (1972) found that cotton cloth soaked in either carbon disulfide or sulfur efficiently removed mercury from sediments and laboratory aquaria water. Ilin et al. (1972) showed that an electron ion-exchanger could be prepared specifically for mercury and silver ions when carbon disulfide was used to treat amino group resins. In addition, mercapto cellulose, prepared by sulfuration of surgical cotton with thioglycolate was effective in absorbing mercury ions (Kobayashi et al., 1972). Yokota et al. (1971) showed that charcoal activated with dithizone sulfurizing agent would remove mercuric chloride in the presence of excess chloride.

Humenic and Schnoor (1974) in an attempt to improve mercury (II) sorption by activated carbon employed various chelating agents and carbon capacities to sorb mercury were observed to increase seven fold in batch isotherm tests and nearly fourteen fold in column tests at lowered pH. Water soluble chelates, APDC (Ammonium 1-pyrrolidine dithiocarbamate) and TETA (Triethylene tetraamine) significantly increased the removal of mercury by activated carbon at pH 10. Removal of mercury by carbon disulfide treated activated carbon improved and was found to be independent of mercury concentrations. This work indicates that the treatment of activated carbon with a sulfurizing agent to form chelating

groups on the carbon improves mercury removal from water and wastewater.

Thiem et al. (1976) treated aqueous solutions of mercury by activated carbon in presence of various combinations of EDTA, tannic acid, citric acid and calcium. Samples close to neutral pH produced the most effective treatment; quite small amount of tannic acid dramatically increased treatment success as did progressively higher concentration of calcium ions.

III. SCOPE OF THE INVESTIGATION

From a survey of the literature it is apparent that there already exists a natural background of mercury in almost all surface and ground waters. Any further addition of mercury from man-made sources is bound to increase this background to a level which may be of concern because of probable entry of mercury into the food chain apart from possible direct ingestion. Consequently, removal of mercury from industrial wastewater is important so as to control addition of mercury into natural bodies of water through such waste discharges. Equally important is the removal of mercury during water treatment when the level in the raw water supply may exceed the permissible limit.

All water and wastewater treatment processes remove mercury to some extent. However, there is a need to improve the efficiency of these processes as well as to explore the potential of raw material/processes for removing mercury from water and wastewater. Activated carbon is the most commonly used sorbent for removal of organic and inorganic contaminants from aqueous environment. However, its high capital and regeneration costs have led to a search for suitable alternative materials even in the advanced countries. Coal, one of the raw materials used in the manufacture of activated carbon has been investigated as a potential sorbent for removing heavy metals and pesticides from water with varying degrees of success (King et al., 1969; Manahan, 1975).

It seems appropriate to evaluate the potential of coal as a sorbent for removing mercury from water and wastewater. Availability of coals in India with high sulfur content adds another plus point for evaluating Indian coals in this respect. Data related to the effect of various relevant physical and chemical system parameters on mercury removal by coal together with an understanding of the sorption interaction may contribute significantly to the development of a coal based process for removal of mercury from water and wastewater. The present study was undertaken along the following lines:

1. screening a number of Indian bituminous coals in terms of their suitability in removing mercury in comparison to activated carbons.
2. batch sorption tests to evaluate the important sorption parameters for mercury removal using the most suitable bituminous coal,
3. effect of various system parameters on sorption, e.g., pH, temperature, sorbent size, stirring rate, chloride and calcium concentration so as to be able to understand the sorption interaction, and
4. improving the sorption capacity through chemical pretreatment of the coal.

The second phase of the study was devoted to downflow coal column studies for removing mercury from water with or without clay turbidity, when mercury was present with turbidity, alum coagulation followed by sedimentation preceded column operation. The objective of this phase of the study was to simulate plant conditions.

IV. MATERIALS AND METHODS

A. Materials

1. Sorbents and Preparation

Two samples of activated carbon (Filtrisorb 400, manufactured by Calgon Corporation, Pittsburg, U.S.A., and Laxmi Carbon, manufactured by Laxmi Carbon, Nazimabad, India) and four samples of bituminous coals from different locations, viz., Giridih, Makum, Margherita and Singareni were used as sorbents in this study. Giridih coal was obtained through the Water Treatment Division, National Environmental Engineering Research Institute, Nagpur while the others were obtained directly from the respective coal fields. All sorbents were pulverized, sieved to a geometric mean size (G_m) of 357 μm , washed in distilled water to remove the fines and other adhered impurities, dried at 103°C, dessicated and stored in tightly stoppered plastic bottles for use in sorption experiments. Sorbent size other than 357 μm were also used in some experiments. The proximate and ultimate analysis of the four coal samples are shown in Tables 5 and 6 respectively. These analyses were obtained from the Central Fuel Research Institute, Dhanbad. The physical properties of the Giridih bituminous coal sample are shown in Table 7.

2. Mercury and Chemicals

All chemicals used were of analytical reagent grade. Stock mercury solution (1 g/l) was prepared from analytical reagent

Table 5
Proximate Analysis of Coals

		Giridih	Singareni	Makum	Margherita
Moisture*	%	4.6	7.1	1.2	1.8
Ash	%	18.8	14.3	6.3	6.0
Volatile	%	31.6	24.5	41.7	40.3
Fixed carbon	%	45.0	54.1	50.8	51.9

* At 60% R.H., 40°C

Table 6
Ultimate Analysis of Coals

		Giridih	Singareni	Makum	Margherita
Moisture*	%	4.60	7.10	1.20	1.80
Ash	%	20.68	15.73	6.93	6.60
Carbon	%	61.62	65.31	74.27	74.67
Hydrogen	%	3.38	3.40	5.20	5.23
Sulfur	%	0.33	0.44	2.70	0.09
Nitrogen	%	1.31	1.31	1.17	1.25
Oxygen (by difference)	%	8.08	6.71	8.53	8.36

* At 60% R.H., 40°C

Table 7

Physical Properties of Giridih Bituminous Coal

Parameters	Range of Values	Values for Giridih Coal	Remark
1. Specific gravity	1.3-1.5	1.33	AWWA specifies 1.55 for anthracite
2. Moh's hardness	Around 3	2-3	AWWA specifies 3-3.75 for anthracite
3. Durability test (percent loss in weight after 100 hr of backwashing)	0.63-4.87	0.63	Comparable to that of anthracite
4. Solubility in dilute hydrochloric acid (10% V/V)	Generally less than 2%	0.69	Anthracite is generally inert
5. Sphericity	0.63-0.79	0.74-0.76	Recommended minimum value for filter media is 0.6
6. Phenol leaching	Not detectable	Not detectable	Permissible limit in drinking water is 0.001 mg/l

Adapted from Paramasivam et al. (1973).

grade mercuric chloride and this was used to prepare working mercury solutions for daily experimental work.

3. Water

Water used in all batch sorption experiments was laboratory distilled water redistilled using a glass distillation unit.

Average specific conductivity of this water was 2.9 siemens/cm.

Tap water was used to prepare the raw water for the coal column studies. An analysis of the tap water is shown in Table 8.

Table 8
Analysis of Tap Water

1. pH	7.8 - 8.2
2. Alkalinity	450 mg/l as CaCO_3
3. Hardness	220 mg/l as CaCO_3 , Ca^{++} as $\text{CaCO}_3 = 50 \text{ mg/l}$
4. Chloride	20 mg/l as Cl^-
5. Total dissolved solids	440 mg/l
6. Specific conductivity	800-900 μ siemens/cm
7. Turbidity	Not detectable

4. Glassware

All glassware used in the present study was of 'Pyrex' quality manufactured by Borosil Glass Works Ltd., Bombay and marketed under the brand name 'Corning.' The glassware was soaked overnight in a 10 mg/l of mercury solution to minimise the possibility of mercury adsorption by glass as suggested by Masri and

Friedman (1973). The excess mercury was washed off with nitric acid and distilled water prior to use. It was expected that this procedure would effectively block the active sites on the glass so that additional mercury would not be adsorbed. After a sorption experiment all glassware was soaked in a nitric acid bath for four hours to remove excess mercury and then washed with tap water before soaking in the 10 mg/l mercury solution.

5. Chemical Treatment of Coal

Coal was subjected to various pretreatment, viz., sulfonation, nitric acid oxidation and sulfurization with a view to increase its mercury sorption capacity.

Sulfonation of coal was carried out using sulfuric acid as sulfonating agent with silver sulfate as catalyst (Michelsen et al., 1975). The sulfonation reaction was performed in a one litre beaker using 100 g of coal, 600 ml of concentrated sulfuric acid and 14 g of silver sulfate. The content was stirred intermittently and temperature was maintained at 90°C for 12 hr. Since the reaction resulted in partial decomposition, coal of size larger than 357 μm geometric mean size was used. After the reaction, the black supernatant was decanted and coal particles were washed several times with glass distilled water until the wash-water was clear. This sample was then dried at 103°C, sieved to a geometric mean size of 357 μm , dessicated and stored.

Nitric acid oxidation of coal was accomplished using a medium of 6 M nitric acid with air bubbled through the reaction mixture (Manahan, 1975). Air was introduced into the system to ensure

sufficient oxidation and to enhance the reaction rate. Coal particles, approximately 100 g, were placed in a beaker and 150 ml of glass-distilled water was added to form a slurry. Next, concentrated (12 M) nitric acid was added dropwise using a burette to a maximum volume of 150 ml, resulting in a medium with a final concentration of 6 M nitric acid. Air was introduced into the reaction mixture by bubbling through a glass tube and the reaction was allowed to continue for 12 hr. Since the reaction was extremely vigorous and large volume of NO_2 was liberated, it was carried out in a hood. Similar to the sulfonation reaction, this reaction also resulted in partial decomposition of the coal particles. Hence coal of size larger than 357 μm geometric mean size was also employed here and finally sieved to a geometric mean size of 357 μm as before and stored.

Sulfurization of coal was accomplished by soaking the coal particles in carbon disulfide at room temperature (Humenic and Schnoor, 1974). When the evaporation of carbon disulfide was complete, the coal particles were washed to remove any visible sulfur particles, air dried, dessicated and stored.

B. Methods

1. Analysis of Mercury

In the initial phase of the study, dithizone-mercury complex extraction method as suggested by Elly (1973) was used as a mercury analyzer was not available at that time. Very shortly a mercury analyzer based on flameless atomic absorption principle

was procured and this instrument was used for mercury analysis for a major part of the study. The procedures are outlined below.

a. Dithizone Procedure

Mercury is determined by extraction of mercuric ion with a chloroform solution of dithizone in 1 N sulfuric acid solution. At this reduced pH interference by other metals as lead, cadmium, zinc, nickel, cobalt and iron is minimised. Addition of acetic acid stabilises the mercury-dithizone complex for atleast 1 hr. Bear's law is observed over a concentration range of 0.002 to 0.40 mg/l of mercury (II).

Standard mercury (II) solution (0.1 percent) is prepared by dissolving 1.354 g of analytical reagent grade mercuric chloride (Pfizer Ltd., Bombay) in 1000 ml of 1 N sulfuric acid. From this solution of mercury (II) working dilutions are prepared in glass-distilled water. Dithizone (0.1 percent) is prepared by dissolving 0.5 g of analytical reagent grade dithizone (E. Merck (India) Private Ltd., Bombay) in reagent grade chloroform and diluted to 500 ml and refrigerated. From this stock solution working solutions of 0.001 percent are made in chloroform whenever needed.

A water sample containing mercury is diluted to 500 ml with glass-distilled water and is transferred in a 1000 ml separatory funnel to which 14 ml of concentrated sulfuric acid are added, mixed and allowed to cool to room temperature. To this solution are added 40 ml of 6 N acetic acid and 5 ml of chloroform and agitated vigorously for one minute. The phases are allowed to separate and the chloroform layer is withdrawn and discarded.

Ten ml of 0.001 percent dithizone solution are added and mixed thoroughly for one minute. Phases are again allowed to separate and the mercury-dithizone complex is withdrawn. The colour intensity of this complex is measured at 500 nm against a reagent blank using a Spectronic-20 spectrophotometer. A standard curve for mercury is shown in Fig. 3.

In the absence of mercury (II), no significant colour is extracted into dithizone while mercury (II) produces an orange colour in the organic layer, the colour becoming more pronounced with the concentration. Organic mercury compounds are not extracted by dithizone unless they are converted to mercury (II) by a digestion process.

b. Flameless Atomic Absorption Procedure

A mercury analyzer (Coleman MAS-50, Perkin-Elmer Corporation, Maywood, Ill., U.S.A.) based on the method developed by Hatch and Ott (1968) was employed for mercury measurement. The operating characteristics of the instrument are as follows:

Sensitivity : equal to or better than 0.01 μg of mercury

Range : 0 to 9 μg without dilution

Response time : less than one minute over the entire scale range

In the procedure, 100 ml of sample is treated with nitric and sulfuric acids in the presence of excess potassium permanganate to oxidise all the mercury present to the mercuric (Hg^{++}) form. The excess permanganate is reduced by hydroxylamine hydrochloride and then the mercury is reduced to metallic mercury with stannous

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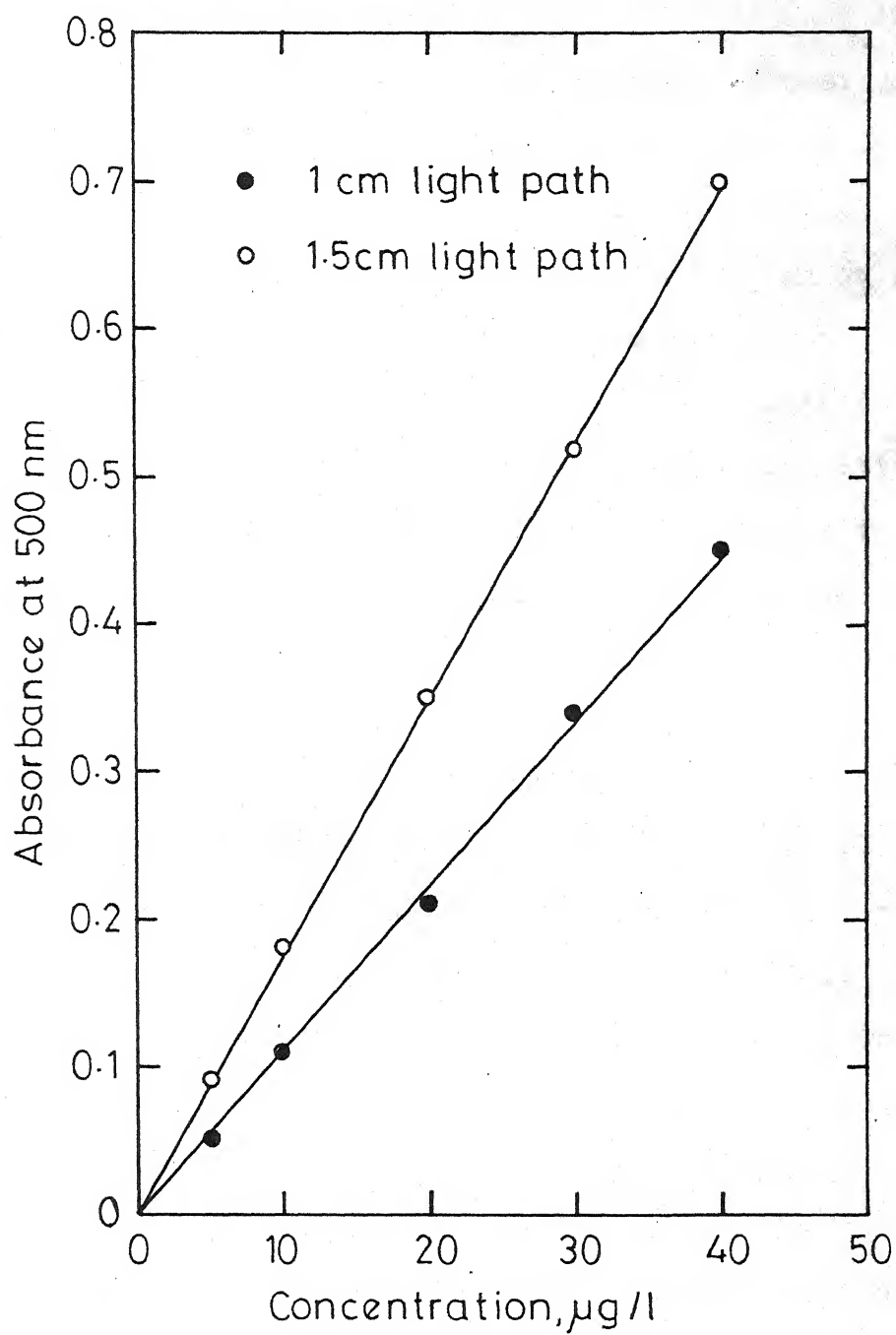


Fig. 3 - Standard Curve for Mercury.
(Dithizone Method)

chloride. An aerater is placed in the reduced mercury solution. A pump circulates the air in the closed loop system through the solution and the air evaporates the mercury and carries it through the absorption cell. The mercury vapour which is in atomic form, absorbs the 253.7 nm radiation emitted from the light source (hence, the term, 'flameless atomic absorption'). The change in energy transmitted through the cell is detected by a UV-sensitive phototube. A narrow bandpass filter is in front of the phototube permits transmission of only the 253.7 nm radiation and makes the analyzer insensitive to visible rays.

2. Zeta Potential of Coal

Effect of pH on the zeta potential of coal was studied using a Zetameter (Zetameter Inc., New York). To facilitate the measurement the coal sample was powdered and the fines of colloidal size suspended in glass-distilled water were employed. In order to vary the initial pH of the system potassium hydroxide or nitric acid was used as required.

3. Experimental Techniques

Batch sorption tests were used to screen the most suitable coal for mercury sorption from a number of candidate coal samples in comparison to activated carbon samples. These tests were also employed to study the relevant parameters of the mercury-coal sorption system using the coal sample selected through the screening test.

a. Batch Sorption Tests

The reaction mixture for all batch sorption tests consisted of a total volume of 250 ml containing 1 g/l of sorbent and the desired concentration of mercury. The reaction mixture was placed in a 500 ml stoppered glass bottle and agitated in a rotary shaker. Since the measurement of mercury required a sample volume of 100-250 ml depending upon the mercury concentration and method employed, it was necessary to use a number of identical reaction bottles for each sorption test. At the end of the desired time intervals, bottles were removed from the shaker and the contents analysed for mercury. Temperature and pH of the reaction mixture were measured initially and at the end of the experiment.

Using the most suitable coal selected through the screening experiment, sorption kinetic studies were performed employing different initial concentrations of mercury and samples were analysed after 10, 20, 30, 45 and 60 min, and 2, 4, 6, 8, 12, 24 and 48 hr. Using the time required to obtain equilibrium, sorption tests were conducted to evaluate the effect of pH on mercury sorption. The reaction mixture was adjusted to various initial pH values using nitric acid and potassium hydroxide. However, to investigate the effect of temperature on the rate of sorption, kinetic studies at different constant temperatures (15, 20, 25 and 33°C) were performed.

b. Desorption and Regeneration Studies

For desorption studies, 250 mg of coal was loaded with mercury using 250 ml of a 100 mg/l solution and a contact time of

24 hr. Experimental conditions were similar to that of the batch sorption tests. The amount of mercury sorbed was determined by measuring the concentration of mercury remaining in solution. The mercury loaded coal was then filtered through a 0.45 μm membrane filter (Millipore Corporation, Bedford, Mass.) and the retained coal was washed gently with glass-distilled water to remove any unsorbed mercury followed by air drying. Mercury was then allowed to desorb by suspending the coal in 250 ml of glass-distilled water with agitation. Similar to the sorption kinetic experiments, several identical bottles containing 250 mg of mercury loaded coal was employed and at various time intervals bottles were withdrawn from the shaker and analysed for desorbed mercury.

For sorbent regeneration studies, the procedure used in the desorption studies for mercury loading was employed. 250 mg of air dried mercury loaded coal was subjected to 250 ml of regenerant solution with agitation for 24 hr. The mercury desorbed was determined. The coal was then filtered through 0.45 μm membrane filter, air-dried and subjected to another mercury loading cycle. The loading-regenerating cycle was repeated several times till the percent recovery (desorption during regeneration) dropped down drastically and the mercury uptake decreased significantly.

c. Mercury Association with Turbidity

Since the majority of the mercury contaminated waters may also contain turbidity, a study was conducted to evaluate the removal of mercury due to its association with turbidity. Mercury association with turbidity was investigated under the different

experimental conditions, viz., constant initial kaolinite turbidity with varying input mercury levels and vice versa. In order to estimate the amount of mercury associated with turbidity, the supernatant mercury concentration of the system was measured after removing the kaolinite turbidity by centrifugation @ 6000xg for 10 min or by alum coagulation with the optimum alum dose for the initial turbidity using a standard jar test procedure (flash mix @ 100 rpm for 1 min and slow mix @ 20 rpm for 15 min followed by 30 min quiescent settling).

d. Column Studies

In order to investigate the practical aspects of mercury removal by coal, downflow column studies were conducted using 10.0 mm glass columns filled with 0.78 mm geometric mean size coal for a height of 45 cm. Turbidity free water containing mercury was fed directly to the column without any pretreatment. However, when mercury was present in association with kaolinite turbidity, alum coagulation followed by sedimentation preceded column operation. The optimum alum dose was predetermined using a standard jar test procedure. Influent and effluent mercury concentrations were monitored with time, zero time being reckoned after the passage of 100 ml of the effluent. Attempts were made to maintain constant flow rates.

V. RESULTS AND DISCUSSION

Results of all experiments are presented in graphical and tabular form. In order to facilitate presentation, a discussion of the results follows each phase of the experimental work. For the most part, only typical results are shown and discussed. Experimental studies which constitute the background for a coal based mercury removal process are presented in the earlier section. This is followed by a discussion of the nature of mercury-coal interaction. The later section includes the studies on the engineering aspects of mercury removal using a coal based process.

A. Selection of Sorbent

Two samples of activated carbon (Filtrisorb 400 and Laxmi carbon) and four samples of bituminous coals (Giridih, Singareni, Margherita and Makum coals) were used as sorbents in the screening experiment to select the most suitable coal for removing mercury from water. Activated carbon was used as a reference to compare the performance of these coals. Kinetics of mercury sorption on these sorbents with initial mercury concentration of 100 $\mu\text{g/l}$ are shown in Fig. 4. In general, for all the sorbents the time required to attain equilibrium mercury sorption was about 12 hr. Filtrisorb 400 and Laxmi carbon were comparable in terms of their initial rate of sorption as well as equilibrium mercury sorption capacities which were 94 and 92 percent, respectively. In the case of coals, the initial rates of sorption for Margherita and

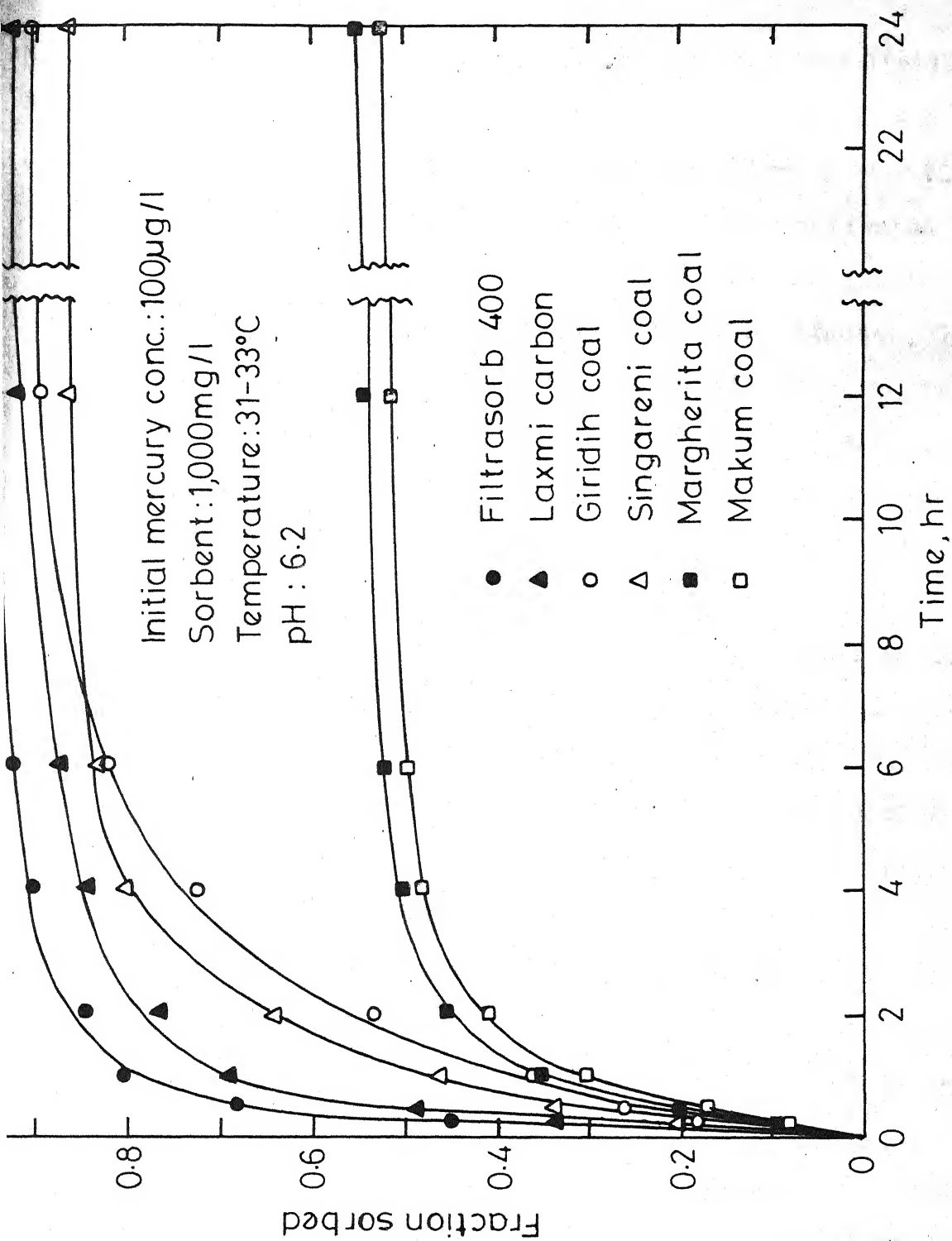


Fig. 4 - Sorption of Mercury on Different Sorbents.

Makum coals were slightly lower compared to that for Giridih and Singareni coals. Among the four coals tested, Giridih and Singareni coals showed very high equilibrium mercury sorption (about 90 percent) and comparable to that of the activated carbons. Margherita and Makum coals exhibited rather low equilibrium mercury sorption (about 54 percent). For all subsequent studies, Giridih coal was selected as the most suitable sorbent and an equilibrium time of 24 hr was employed. Another reason for preferring Giridih coal over Singareni coal was the availability of considerable amount of data on the use of this coal in water treatment (Paramasivam, 1972; Oza, 1974 and Sriramulu, 1975).

It is reasonable to expect that coals with higher sulfur content would be more efficient in removing mercury due to a strong affinity of mercury for sulfur. Surprisingly, the coals with the higher sulfur content (Margherita and Makum) showed lower mercury sorption. The reason for this may be attributed to the form in which the sulfur is present. While organic sulfur is highly reactive with mercury, inorganic sulfur does not bind mercury so readily. In Margherita and Makum coals the sulfur may be existing as pyrites and occurrence of sulfide possibly leads to the formation of soluble mercury complexes (Reimer et al., 1974). In the case of Giridih coal almost all the sulfur is in organic form (Mukherjee, 1978) which makes it a more potential sorbent of mercury. Presumably, this is also the reason for the high mercury sorption exhibited by Singareni coal.

Although raw bituminous coal does exhibit a small amount of inherent ion-exchange capacity, this capacity decreases from peat to lignite through bituminous coal with the progression in the coalification process i.e., with the increase in carbon content (Manahan, 1975). With the coalification process, there is marked decrease in the hydroxyl and carboxyl group content of the coal accompanied by a corresponding loss of water. Therefore, most of the peripheral carbon structures originally existing as the carboxyl and hydroxyl functional groups are gradually converted to methyl groups and other aliphatic hydrocarbon groupings. These carboxyl and hydroxyl groups impart ion-exchange properties to the sorbent (Manahan, 1975). Lower carbon content of both Giridih and Singareni coals compared to that of Margherita and Makum coals (Table 6) shows that possibly the first two coals had not undergone intensive coalification thus retaining more of the original surface groups contributing to ion-exchange properties. The ash content is also expected to contribute to the ion-exchange properties and higher ash contents of Giridih and Singareni coals (Table 5) make these coals more potential ion-exchanger for removing mercury.

B. Mercury Sorption on Giridih Coal

1. Optimum Rate of Agitation

Before conducting further studies on the Giridih coal-mercury system it was thought appropriate to select the optimum rate of agitation for mercury sorption from the three different speeds available in the rotary shaker used. The experimental

conditions for the batch sorption test were initial mercury concentration 100 $\mu\text{g/l}$; pH 6.2; temperature 30°C; Giridih coal (G_m 357 μm), 1000 mg/l; and reaction time 10 min. The amounts of mercury sorbed were 12, 15 and 16 percent for speeds 20, 40 and 80 rpm, respectively. Mercury sorption increased initially with agitation and beyond a certain rate of agitation the effect was practically negligible. Certain minimum agitation would be necessary to take care of the bulk diffusional resistance which in the present experimental system was 40 rpm. All subsequent sorption experiments were conducted with this speed.

2. Sorption Kinetics

The two important physicochemical aspects for parametric evaluation of the sorption process as a unit operation are the kinetics and equilibria of sorption. Kinetics of sorption describing the solute uptake rate which, in turn, governs the contact time is one of the important characteristics defining efficiency of sorption.

The uptake of mercury by Giridih coal with time is presented in Fig. 5A and 5B. The equilibrium was attained in 24 hr and in all subsequent studies agitation was terminated after this time. It is evident that the rate of sorption which was very rapid initially, decreased markedly between 2-4 hr and gradually approached equilibrium. The rate of sorption increased with increasing initial mercury concentration.

A simple, overall sorption reaction is assumed and is of the form:

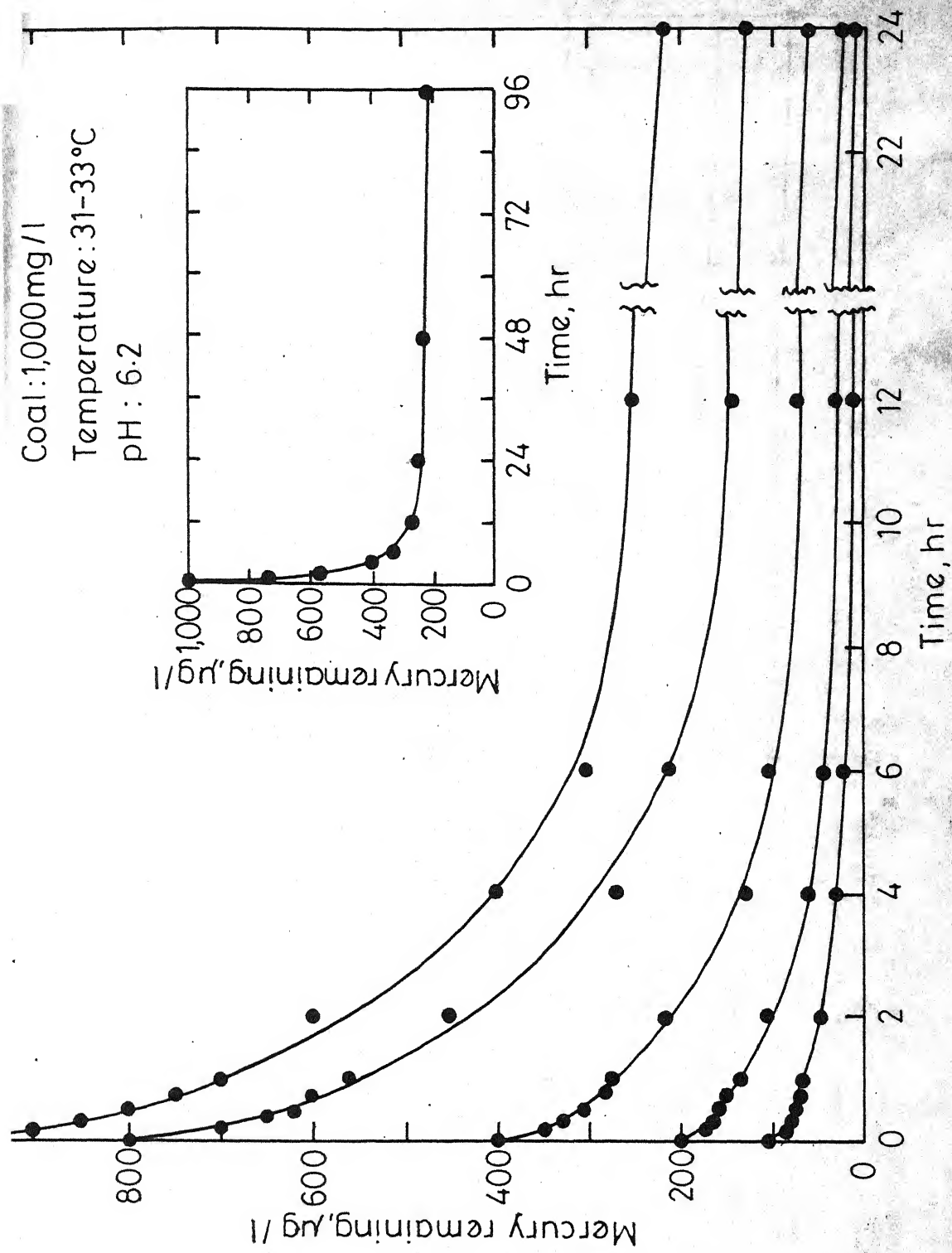


Fig. 5A - Sorption Kinetics of Mercury on Giridih Coal for Different Initial Concentration.

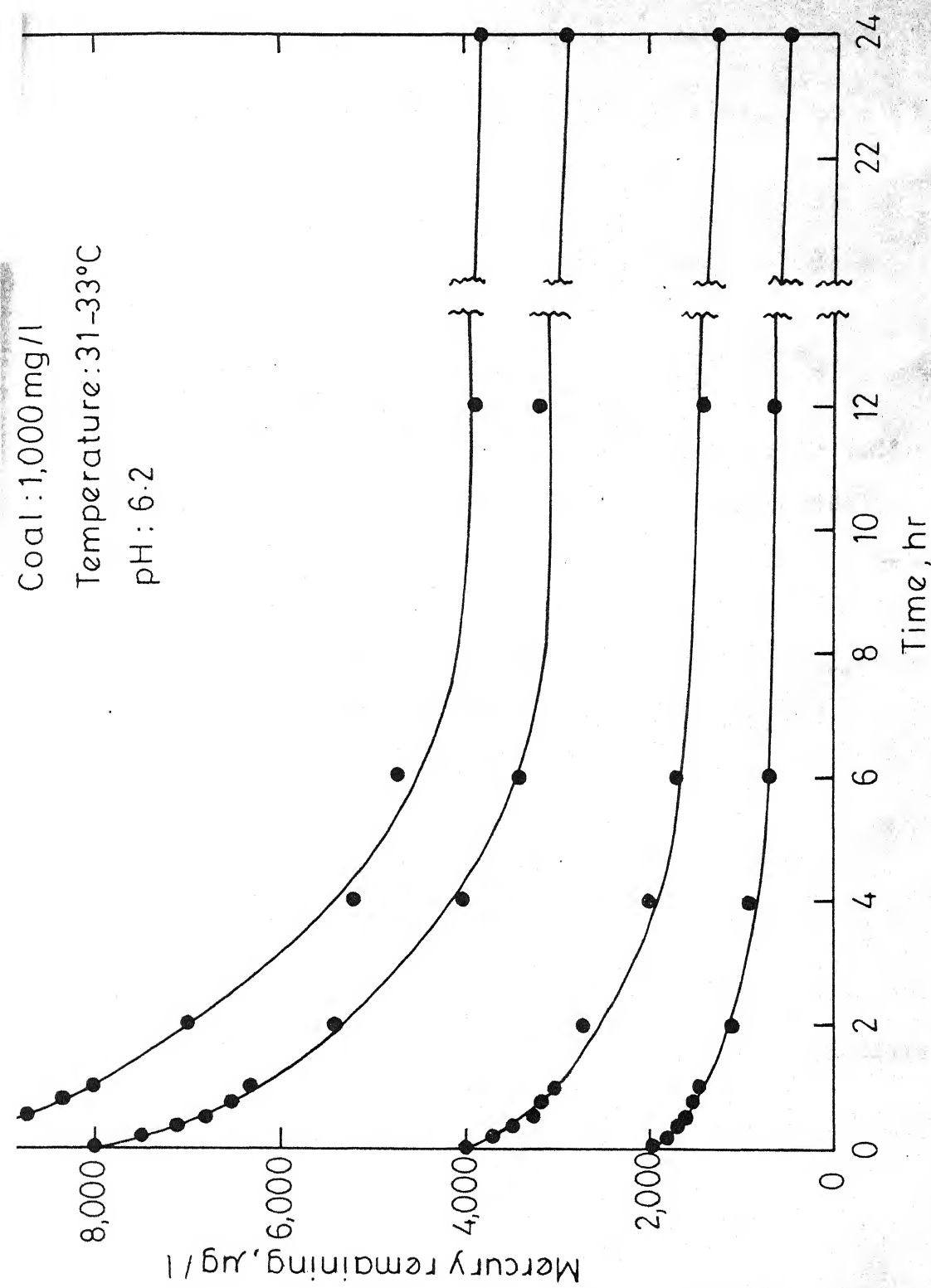


Fig. 5B - Sorption Kinetics of Mercury on Giridih Coal for Different Initial Concentration.



if the first order reversible kinetic model holds true the rate equation for the reaction is expressed as:

$$\begin{aligned} \frac{dC_B}{dt} &= -\frac{dC_A}{dt} = C_{A_0} \frac{dX_A}{dt} = k_1 C_A - k_2 C_B \\ &= k_1 (C_{A_0} - C_{A_0} X_A) - k_2 (C_{B_0} + C_{A_0} X_A) \end{aligned} \quad (2)$$

where, C_{A_0} = initial concentration of mercury in solution,
 C_{B_0} = initial concentration of mercury on coal,
 C_A = concentration of mercury remaining in solution at any time t ,
 C_B = concentration of mercury on coal at any time t ,
 X_A = fractional conversion of mercury, and
 k_1, k_2 = rate constants.

At equilibrium, $k_1 = k_2$ and $\frac{dC_A}{dt} = 0$. Hence

$$X_{A_e} = \frac{K_c - C_{B_0}/C_{A_0}}{K_c + 1} \quad (3)$$

where, X_{A_e} = fractional conversion of mercury at equilibrium, and
 K_c = equilibrium constant

$$= \frac{C_{B_e}}{C_{A_e}} = \frac{C_{B_0} - C_{A_0} X_{A_e}}{C_{A_0} - C_{A_0} X_{A_e}} = \frac{k_1}{k_2} \quad (4)$$

where, C_{A_e} = equilibrium concentration of mercury in solution,
and

C_{B_e} = equilibrium concentration of mercury on coal.

The rate equation in terms of equilibrium conversion can be obtained from equations (2), (3) and (4)

$$\frac{dX_A}{dt} = (k_1 + k_2)(X_{A_e} - X_A) . \quad (5)$$

Integration of equation (5) gives

$$- \ln\left(1 - \frac{X_A}{X_{A_e}}\right) = k_1\left(1 + \frac{1}{K_c}\right)t . \quad (6)$$

The equation (6) can be written in a different form with more physical meaning as follows:

$$\ln [1 - U(t)] = -k't \quad (7)$$

$$\text{where, } k' = k_1\left(1 + \frac{1}{K_c}\right) = k_1 + k_2 \quad (8)$$

and

$$U(t) = \frac{C_{A_o} - C_A}{C_{A_o} - C_{A_e}} = \frac{X_A}{X_{A_e}} . \quad (9)$$

$U(t)$ is called the fractional attainment of equilibrium (Helfferich, Friedlich, 1962).

Plots of $\ln [1 - U(t)]$ vs. time (equation 7) were prepared (Fig. 6A and 6B) using the sorption kinetics data of Fig. 5A and 5B and straight lines were obtained justifying the validity of assuming first order reversible reaction. Similar linearised plots were made for studying the effects of temperature on sorption and are presented in a later section.

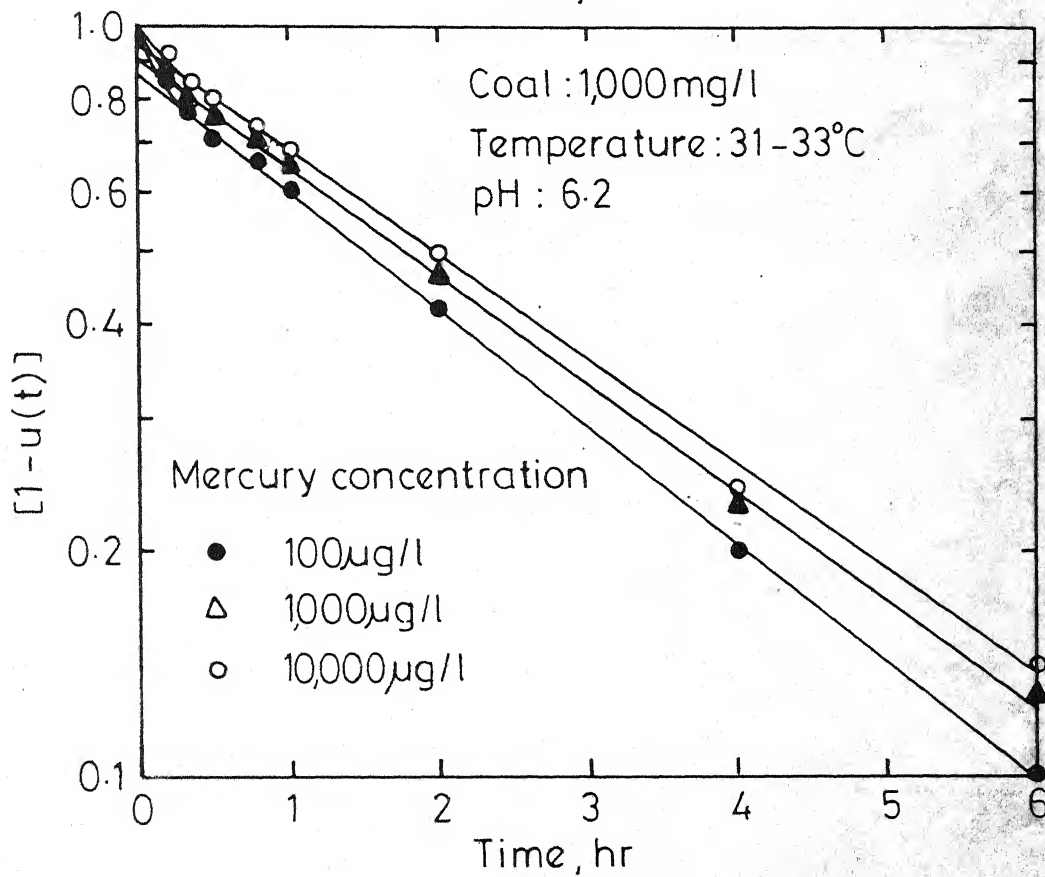
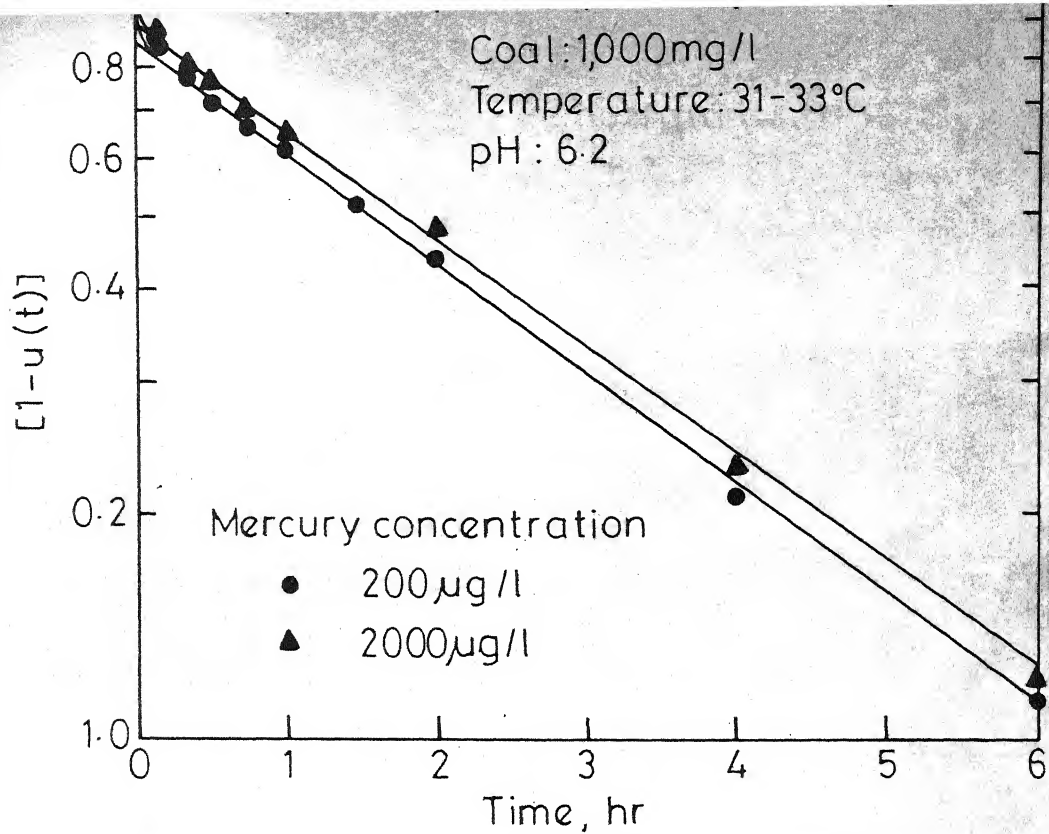
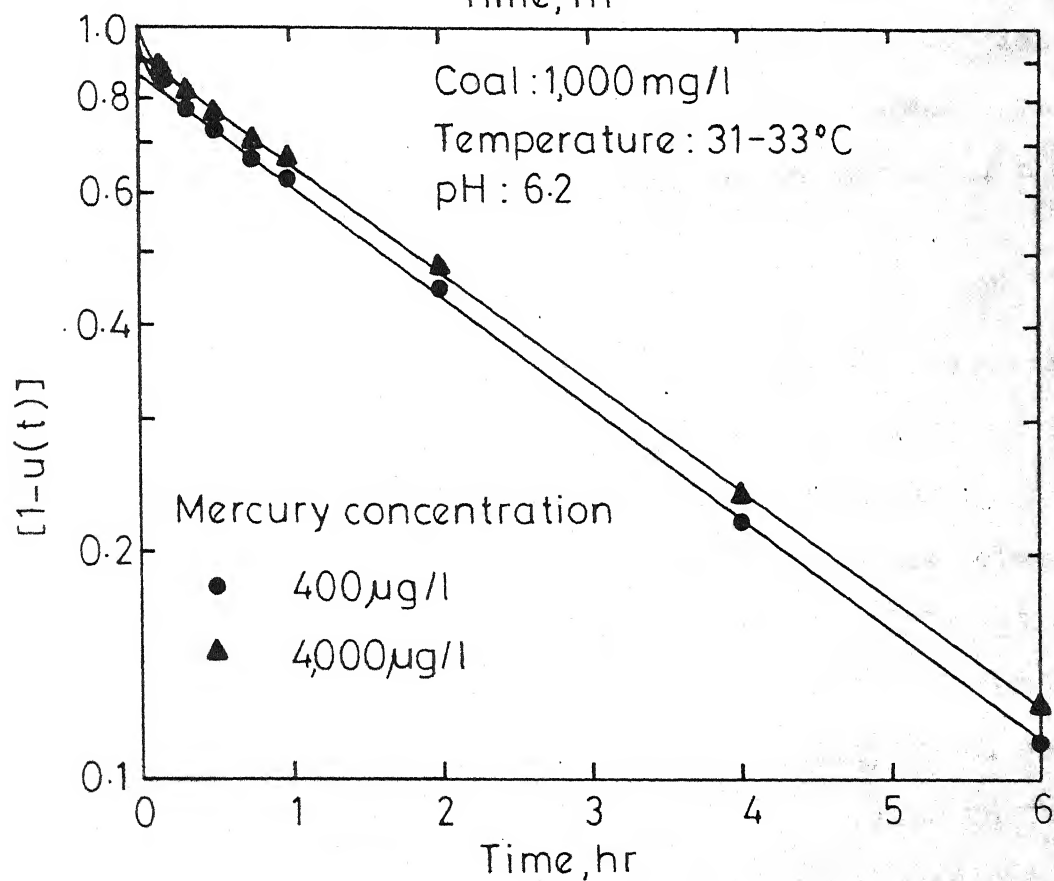
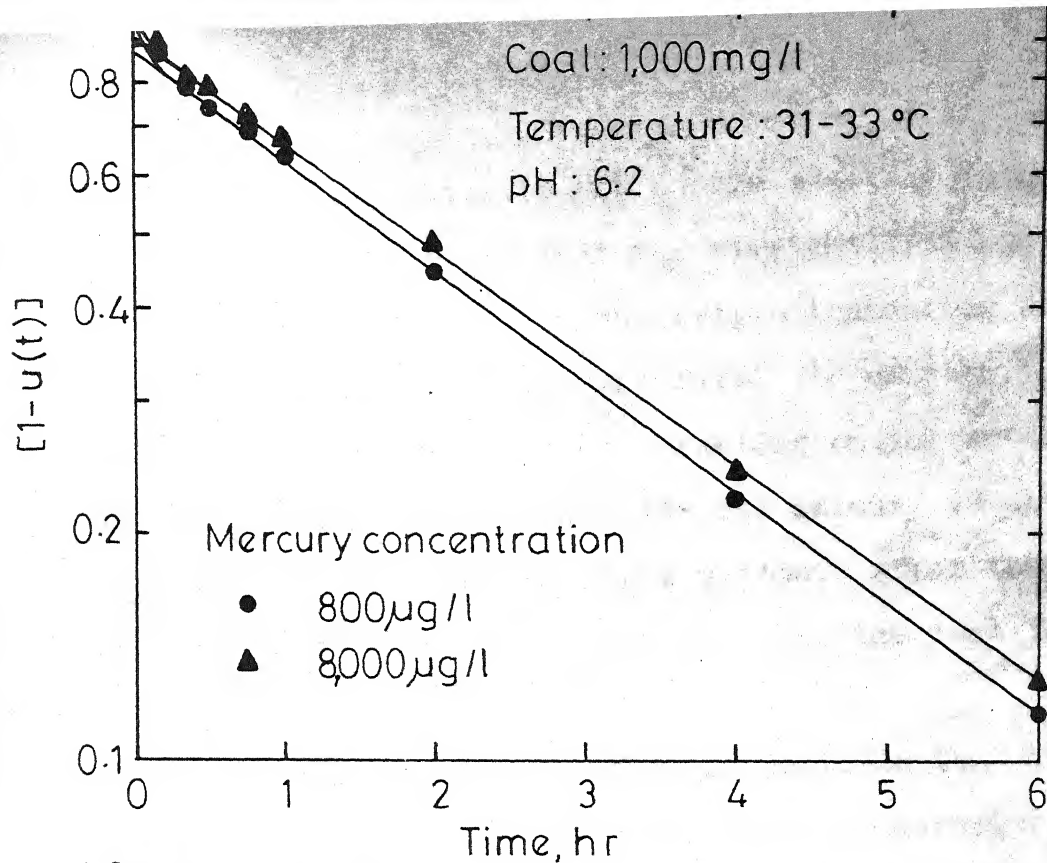


Fig. 6 A - First Order Reversible Kinetic Fit of Mercury Sorption Data on Giridih Coal.



ig. 6 B - First Order Reversible Kinetic Fit of Mercury Sorption Data on Giridih Coal.

From the first order kinetic fit of the sorption data (Fig. 6A and 6B) it may also be noted that the straight line portions when extended did not pass through the origin indicating an initial high rate of mercury uptake during the first few minutes. This was probably due to some active sites existing on the external surface of the coal having high affinity for mercury as observed by Michelsen et al. (1975) in mercury-hair system. After these surface sites were reacted, mercury had to diffuse into the coal for further reaction.

The sorption kinetics data further demonstrate that the sorption rates increased with increasing initial mercury concentration; however, the variation was not a linear one. Another observation is that a greater fraction of mercury was sorbed in a specified time when the initial concentration was lower comparatively.

3. Sorption Equilibria

Saturation curve for mercury sorption onto Giridih coal is presented in Fig. 7, which shows a saturation capacity of 11.0 mg of mercury per gram of Giridih coal of 357 μm geometric mean size at pH 6.2 and temperature 31-33°C. The curve falls between L_2 and H_2 curve according to Giles classification (Giles et al., 1960). An isotherm of this shape can be fitted by Freundlich equation (Kippling, 1965). L curves are usually found when there is no strong competition from the solvent for sites on the surface. H curve is a special case of L curve in which the solute has very high affinity. The sorbed species are often large units, i.e.,

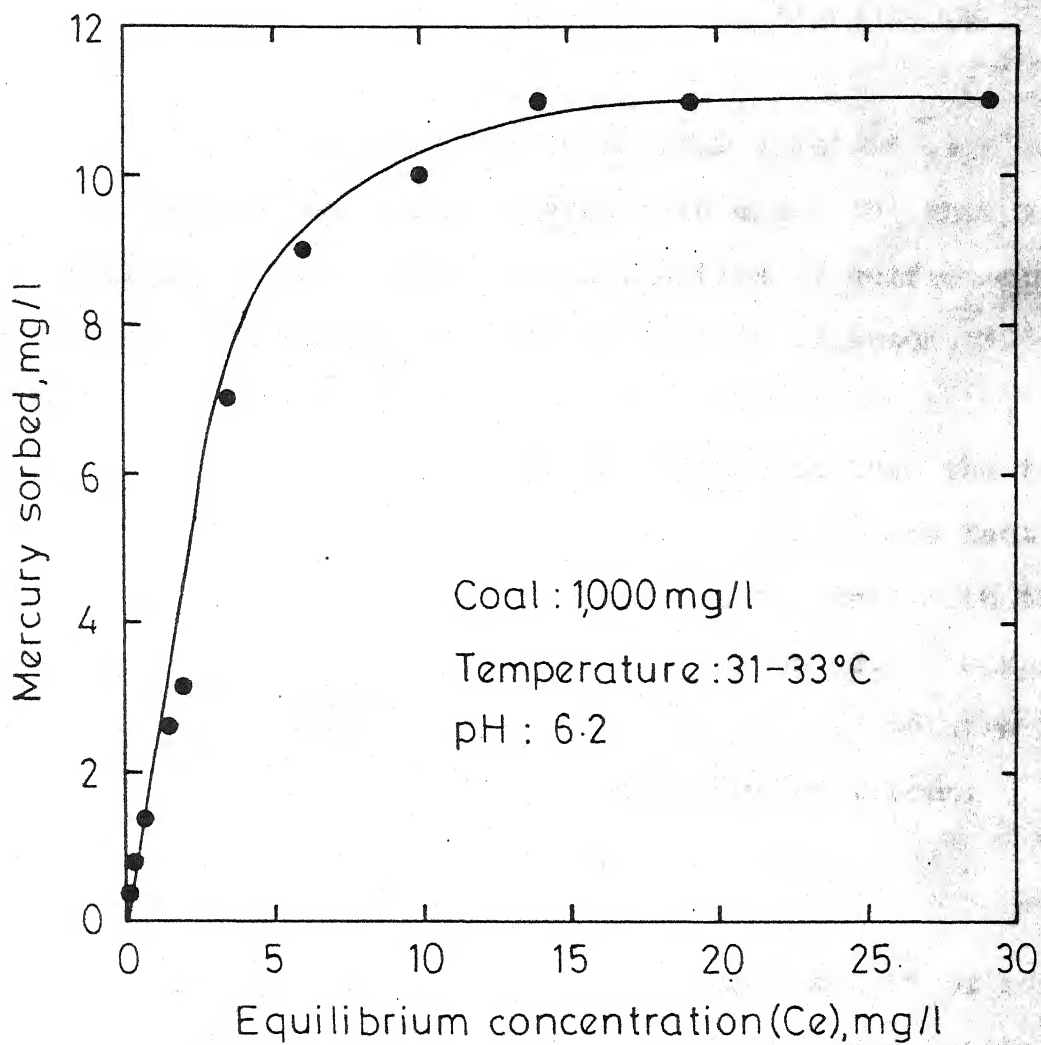


Fig. 7 - Saturation Curve for Mercury Sorption.

ionic micelles but sometimes they are apparently single ions which exchange with other ions of much lower affinity for the surface. This can also result from chemisorption of the solute on the surface.

The Freundlich equation for isothermal sorption is a special case for heterogeneous surface energies in which the energy term in the Langmuir equation varies as a function of surface coverage strictly due to variation in heat of sorption (Adamson, 1967). Although the Freundlich equation has no theoretical basis, it has been found to be more adaptable to sorption data than the theoretically derived Langmuir equation. This is due to the fact that the majority of the sorption processes do not comply with the first assumption on which the Langmuir equation is based. A complete monolayer is not usually formed in the sorption of solutes from solution. The Freundlich equation has the general form:

$$\frac{X}{m} = K C_e^{1/n} \quad (10)$$

where, $\frac{X}{m}$ = weight of mercury sorbed per unit weight of sorbent,

C_e = concentration of mercury remaining in solution at equilibrium, and

K, n = constants.

Data are usually fitted to the logarithmic form of the equation

$$\log \frac{X}{m} = \log K + \frac{1}{n} \log C_e, \quad (11)$$

which gives a straight line with a slope of $\frac{1}{n}$ and an intercept equal to the value of $\log K$ for $C_e = 1$ ($\log C_e = 0$). The

intercept is roughly an indicator of sorption capacity and the slope, $\frac{1}{n}$, of sorption intensity. Freundlich equation generally agrees quite well with Langmuir equation and experimental data over moderate ranges of concentration. Unlike the Langmuir equation, however it does not reduce to a linear form at very low concentration nor does it agree very well with Langmuir equation at very high concentrations, since n must reach some limit when the surface is fully covered.

Figure 8 shows the sorption data for Giridih coal-mercury system fitted to the logarithmic form of the Freundlich equation. The value for $\frac{1}{n}$ is 0.71. Humenic and Schnoor (1974) reported values of $\frac{1}{n}$ as 0.978 (pH 4) and 0.953 (pH 10), respectively for activated carbon-mercury system. Apparently, the intensity of sorption for the present system is lower compared to the activated carbon-mercury system. Sorption isotherm shown in Fig. 8 is also useful in predicting the amount of coal needed in a batch process for producing a desired residual mercury level.

4. Effect of pH

Effect of pH on mercury sorption on Giridih coal is presented in Fig. 9, showing the initially adjusted pH values with potassium hydroxide or nitric acid as required. It was noticed that the final pH values at the end of the 24 hr contact time deviated to various degrees depending upon the initially adjusted values. Apparently this was due to leaching out of hydrogen and hydroxyl ions from the coal. To demonstrate this, an experiment was conducted to observe the change in pH with time for the Giridih

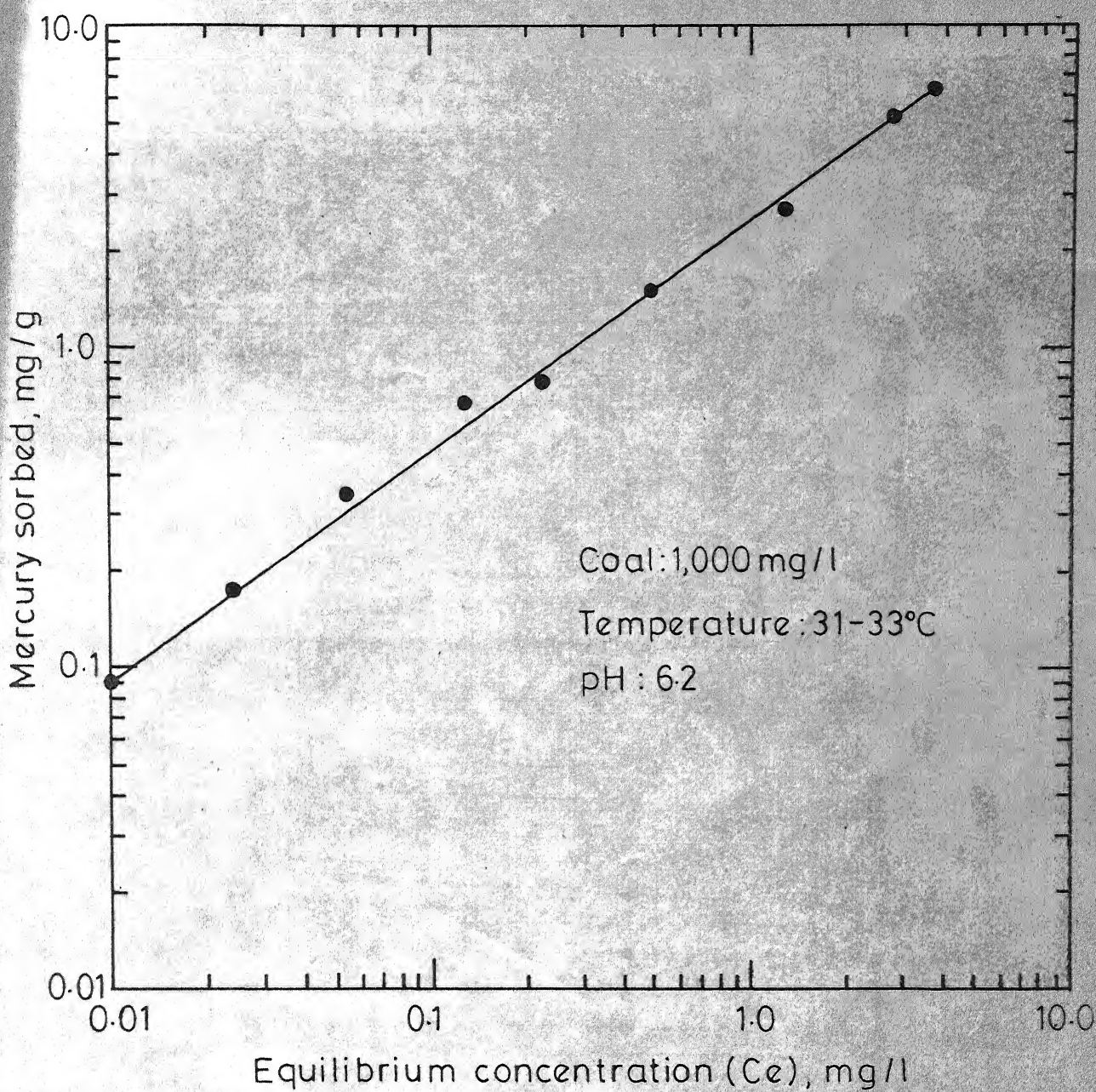


Fig. 8 - Linearised Sorption Isotherm for Giridih Coal.

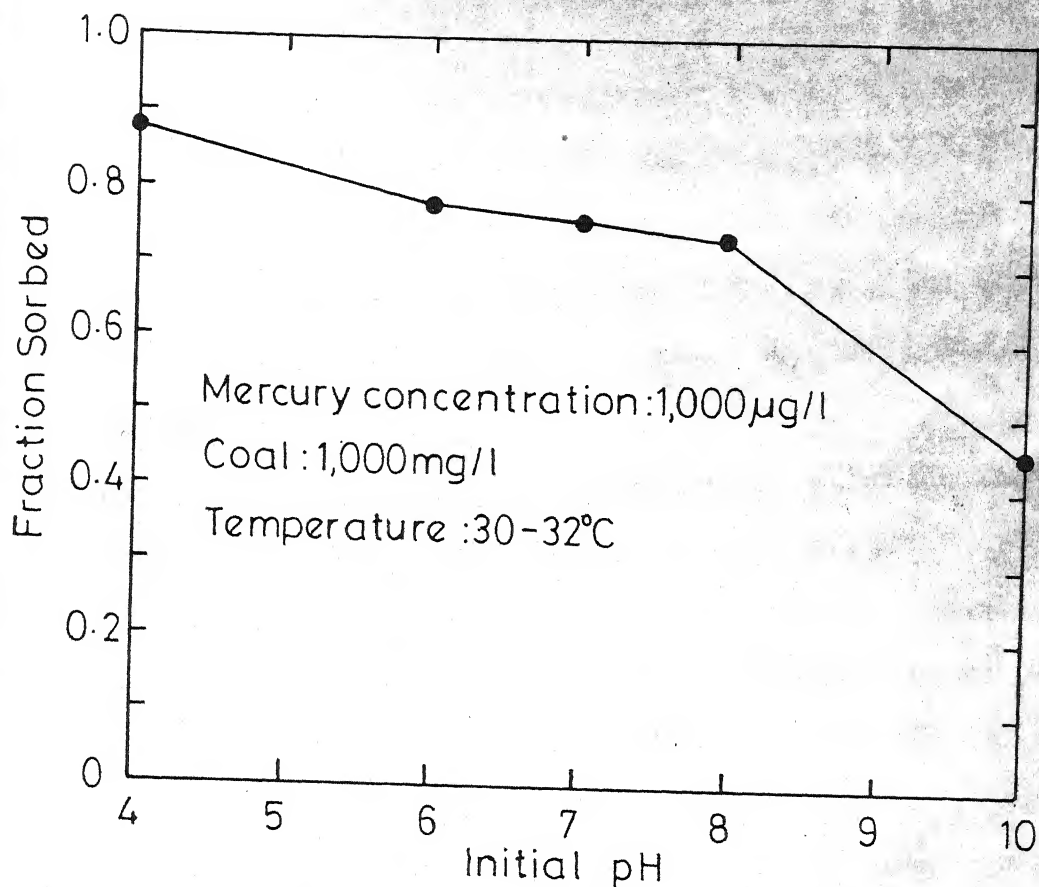


Fig. 9 - Effect of pH on Mercury Sorption on Giridih Coal.

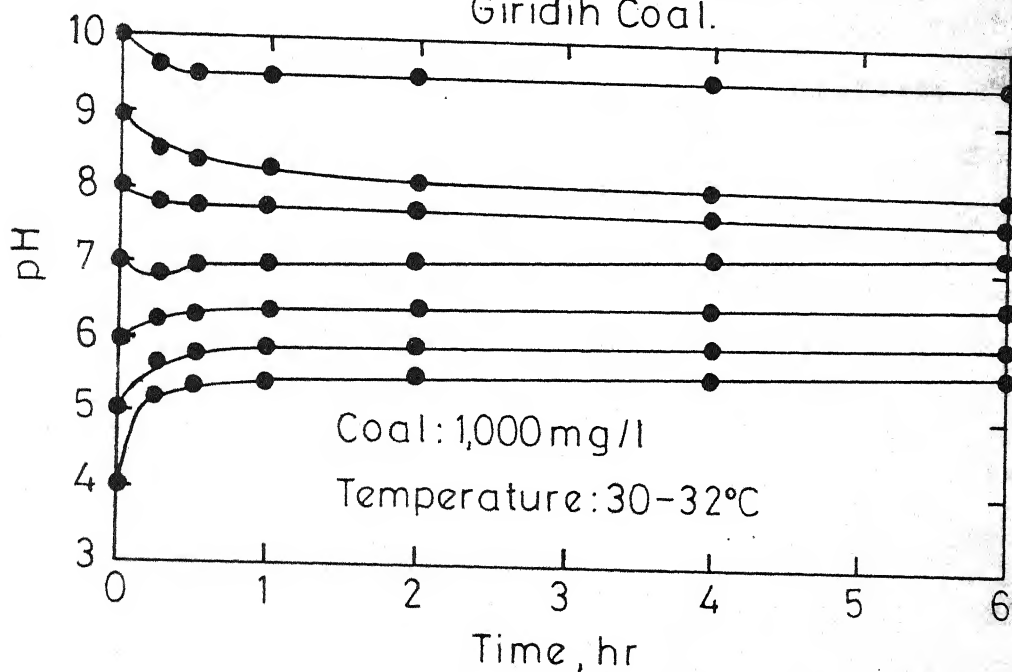


Fig. 10 - pH Change in Giridih Coal-Distilled Water System.

coal-distilled water system against various initially adjusted pH values (Fig. 10). It is seen that the pH of the system fairly stabilised in about one hour. Fig. 9 should be interpreted keeping in mind the pH change. However, due to the presence of buffering capacity in natural water such pH changes are unlikely during mercury sorption.

It is evident from Fig. 9 that mercury sorption decreased with increase in initial pH showing maximum and minimum sorption at the lowest (pH 4) and the highest (pH 10) initial pH values studied. In the pH range 6-8 the fraction sorbed did not change appreciably showing a trend similar to the activated carbon-mercury system (Thiem et al., 1976).

In the present experimental system the mercury species around pH 4 are predominantly Hg^{++} , HgCl^+ and HgCl_2 , the molar ratio of chloride to mercury being two. With the increase in pH the neutral and negatively charged chloro and hydroxo complexes of mercury increase. Between pH 6-8 and at molar ratio of chloride to mercury of two, the predominant species are HgCl_2 and $\text{Hg}(\text{OH})_2$ as well as Hg^{++} and HgCl^+ . With further increase in pH, chloride is substituted by hydroxyl ion and at pH higher than 8 $\text{Hg}(\text{OH})_2$ and the negatively charged species as $\text{Hg}(\text{OH})_3^-$ and $\text{Hg}(\text{OH})_4^{--}$ are formed which might not get readily sorbed as the charge exhibited by the coal surface being of the same nature (Fig. 11). The electrophoretic mobility of the coal was observed to become more negative with increase in pH upto 8 and thereafter the negativity decreased (Fig. 11). Reduction in mercury sorption with increasing pH

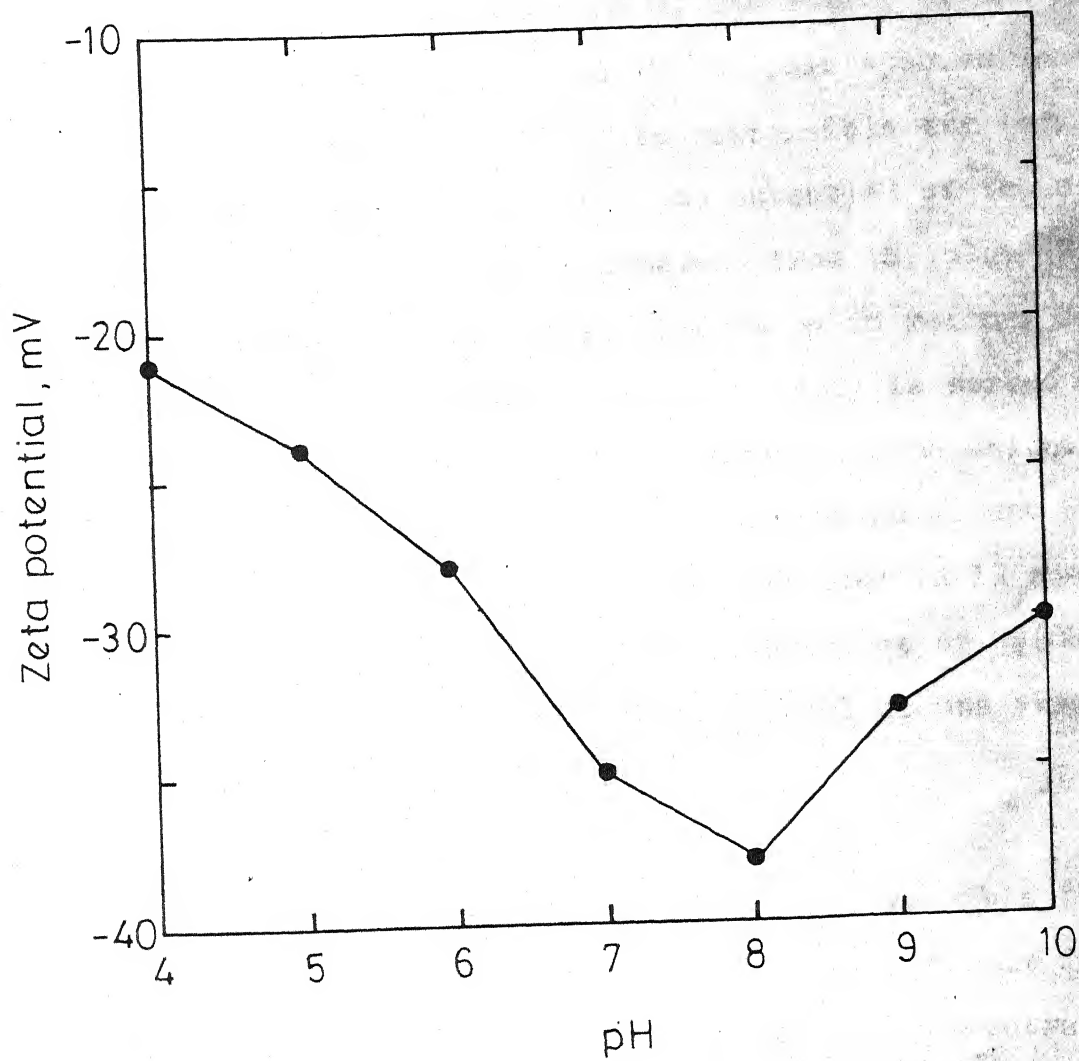


Fig. 11 - Effect of pH on Zeta Potential of Giridih Coal.

seems reasonable as the nature of the mercury species changes from cationic to anionic through neutral and the zeta potential of the coal became more negative. After pH 8, the nature of the mercury species are neutral and anionic and the anionic species increasing further with pH increase. This may be responsible for reduction in mercury sorption even though the zeta potential of the coal became less negative. It is also apparent from the plot (Fig. 9) that although there is a significant reduction in mercury sorption from pH 4 to 10, about 45 percent of the mercury is sorbed at pH 10. Presumably this was due to the presence of some anionic exchange groups on the coal surface like the amine groups as suggested in the literature and further evidenced in IR spectra of coal presented in a later section. Also, presence of $\text{Hg}(\text{OH})_2$ is expected to form hydrogen bonding with hydroxyl groups present on the coal surface (Agarwala, 1978).

5. Effect of Temperature

Linearised sorption kinetic plots for reversible first order reaction of mercury uptake by Giridih coal at four different temperatures and three different initial mercury concentrations are presented in Fig. 12A and 12B. These observations strongly indicated the temperature dependence of the sorption reaction. The rate of mercury sorption increased with temperature. It may also be noted that the linearised plots did not pass through the origin indicating an instantaneous reaction of mercury with active groups on the coal surface followed presumably by intraparticle diffusion as discussed earlier.

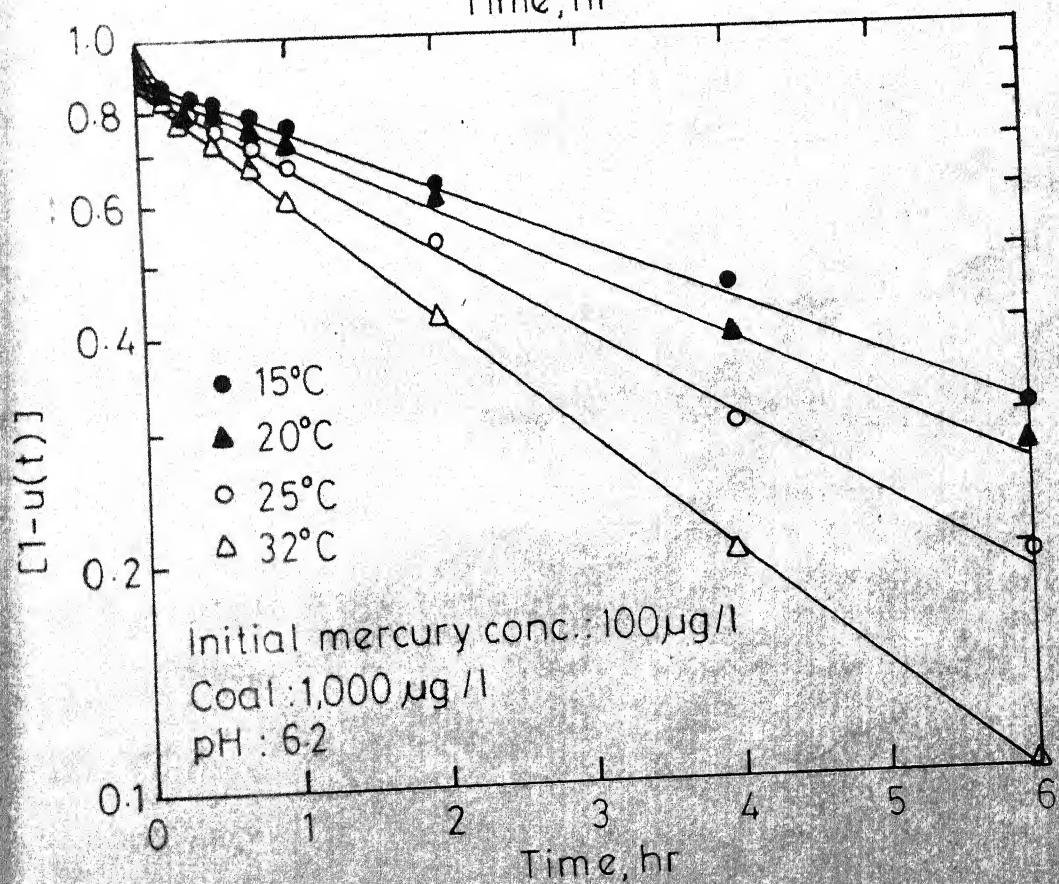
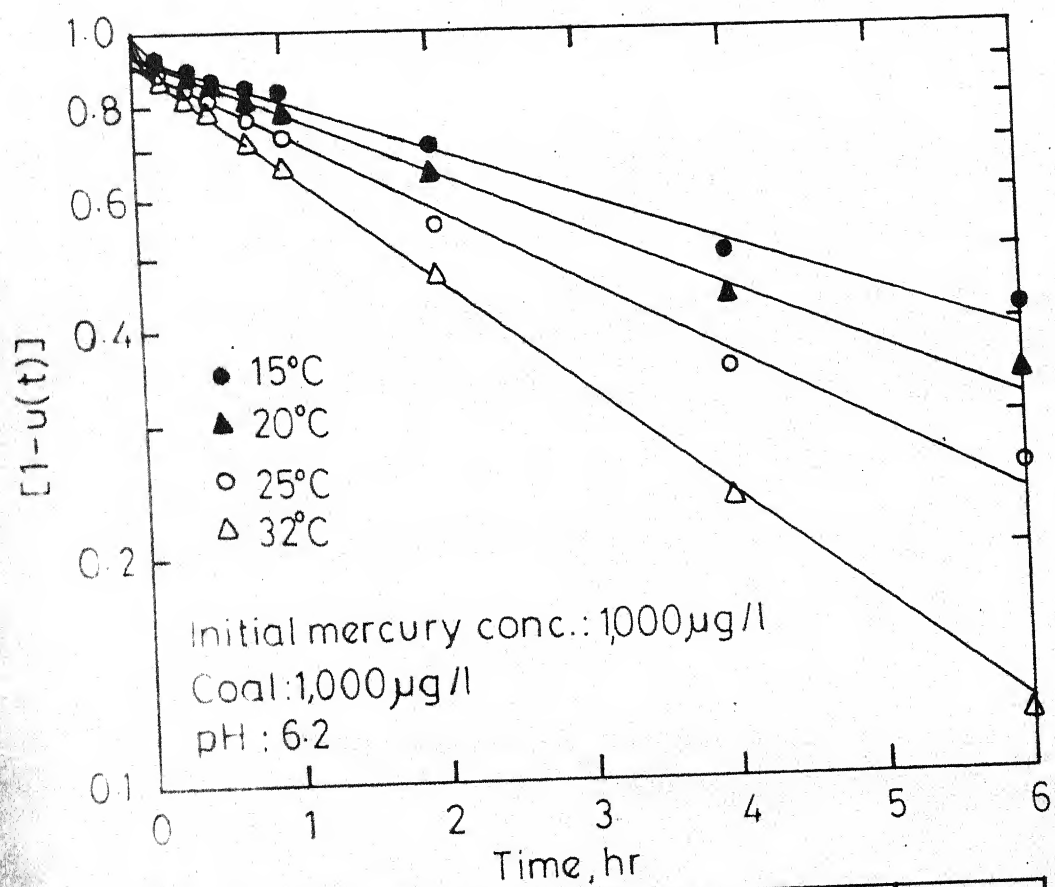


Fig. 12A - Effect of Temperature on Sorption of Mercury on Giridih Coal.

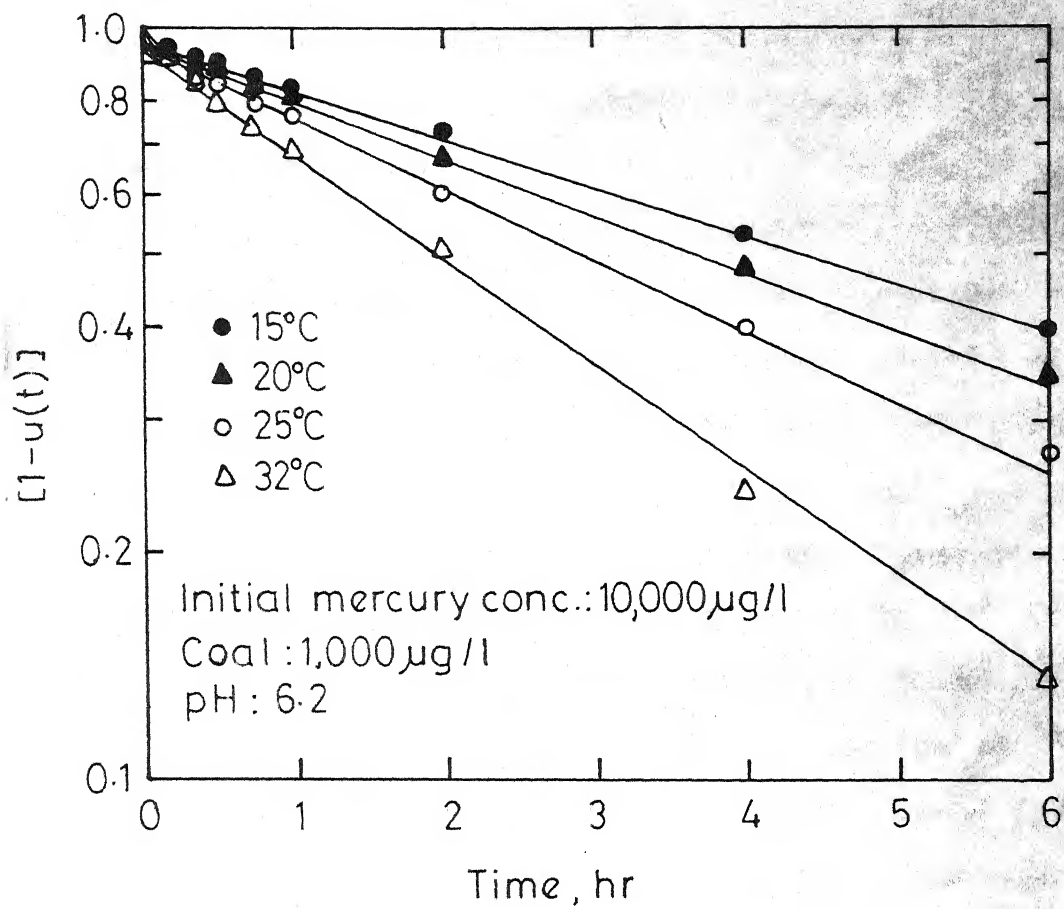


Fig.12B - Effect of Temperature on Sorption of Mercury on Giridih Coal.

Consequent upon significant effect of temperature on the rate of sorption, additional parameters like heat of sorption and activation energy were evaluated using Clausius Clapeyron's and Arrhenius equations, (Table 9) and the average values are 0.91 and 8.39 kcal/mole, respectively. With a view to check the computation, sorption data at different temperatures for initial mercury concentrations were plotted against $t^{1/2}$ (Fig. 13A) as suggested by Morris and Weber (1964) and produced straight lines further supporting intraparticle diffusion of mercury. The logratismis of the slopes of these lines were then plotted against inverse of the temperatures and produced a straight line (Fig. 13B). The value of the activation energy computed using this plot was 7.4 kcal/mole and is comparable to the one obtained from the linearised sorption kinetic plots.

The energy of activation as estimated is high enough for physisorption but not sufficiently high to conclude the reaction as chemisorption (E_a lying between 10-100 kcal/mole). Hydrogen bonding has an effect intermediate between that of chemisorption and physisorption (Kipping, 1965). Activation energy in case of ion-exchange is normally low and lies within 5 kcal/mole. Involvement of an appreciable activation energy is indicative of some specific interactions between the surface groups of coal and mercury. It may be that a combination of several different interactions contribute to mercury sorption which seems quite likely considering the heterogeneous nature of the coal surface.

Table 9

Effect of Temperature on Sorption of Mercury on Giridih Coal

Mercury concentration, $\mu\text{g/l}$	100	1000	10000
Temperatures of sorption,			
Lower, $^{\circ}\text{K}$	288	288	288
Upper, $^{\circ}\text{K}$	306	306	306
Reaction rate constant,			
$k_{\text{lower}}/\text{sec}$	4.27×10^{-5}	3.91×10^{-5}	3.68×10^{-5}
$k_{\text{upper}}/\text{sec}$	10.21×10^{-5}	9.38×10^{-5}	8.42×10^{-5}
Heat of sorption, kcal/mole	0.90	0.95	0.87
Activation energy, $E_a, \text{kcal/mole}$	8.46	8.55	8.16

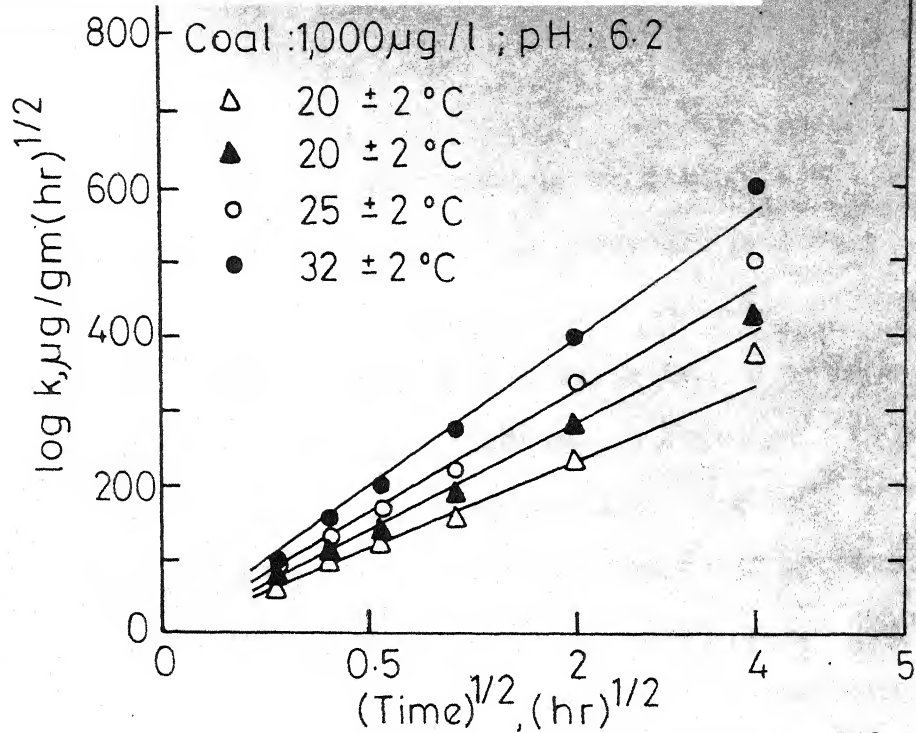


Fig.13 A - A Plot of mercury sorbed vs. $(\text{Time})^{1/2}$ for Giridih Coal-Mercury System.

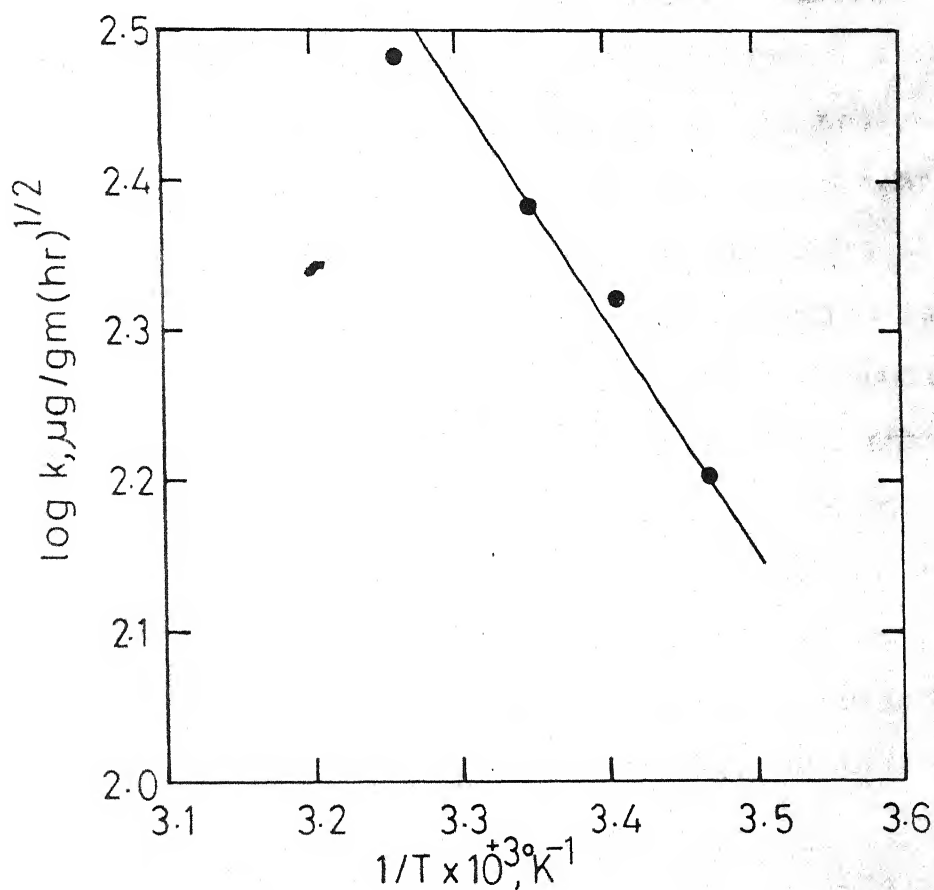


Fig.13B - A Plot of log k vs. $1/T$ for Giridih Coal-Mercury System.

6. Effect of Chloride and Calcium Concentration

A study on the sorption of mercury in presence of chloride ions is significant because mercury forms various chloro complexes depending upon pH and chloride concentration. A wide range of chloride concentration was selected for the study. It was observed that an increase in chloride concentration from 10^{-5} M to 10^{-1} M reduced mercury sorption from 77 to 8 percent at initial mercury concentration of 1000 $\mu\text{g/l}$ (Fig. 14). Reduction in mercury sorption was more pronounced in the chloride concentration range of 10^{-3} M to 10^{-1} M as compared to that in the range of 10^{-5} M to 10^{-3} M. An explanation to this behaviour may be that aqueous mercury solution contains several ionic mercury species varying from cationic to anionic in nature, depending upon the concentration of chloride ions present. At pH 6.2, the pH of the present system and at chloride concentration of 10^{-5} M, the predominant mercury species are Hg^{++} , HgCl^+ , HgCl_2^+ and $\text{Hg}(\text{OH})_2$ which are interacting with the coal surface. As the chloride concentration increases, mercury species change gradually from cationic and neutral to anionic form (HgCl_3^- and HgCl_4^{--}). Apparently, these anionic species were responsible for a pronounced reduction in mercury sorption. This observation also corroborates the data on the effect of pH on mercury sorption already reported. Above pH 8, anionic species, $\text{Hg}(\text{OH})_3^-$ and $\text{Hg}(\text{OH})_4^{--}$ are formed even at lower chloride concentration and these forms were responsible for reduction in mercury sorption.

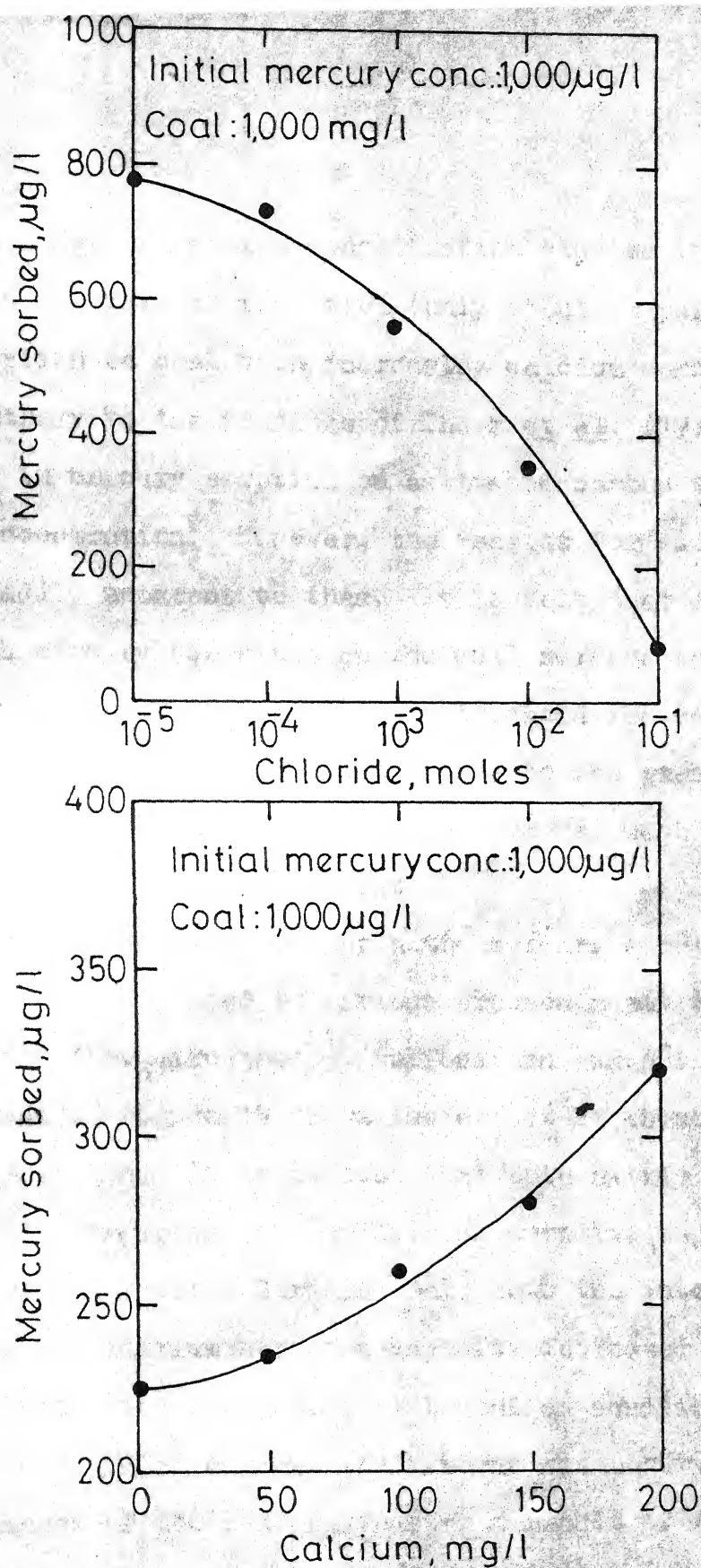


Fig. 14 - Effect of Chloride and Calcium Concentration on Mercury Sorption on Giridih Coal.

In the range of calcium concentration studied (50-200 mg/l) there was no significant reduction (only about 12 percent) of mercury sorption on coal with increasing calcium concentration. This is contrary to the findings of Theim et al. (1976) who observed an increase in mercury sorption on activated carbon with increasing chloride concentration. However, the reasons for such a behaviour were not readily apparent to them. It is felt that calcium might compete with mercury for sites on the coal surface to cause reduction in sorption. The fact that observed reduction in sorption was not significant could be due to the presence of some sites specific for mercury to which calcium was unable to compete.

7. Effect of Coal Pretreatment

With a view to improve upon the mercury sorption efficiency Giridih coal was subjected to various pretreatment, viz., nitric acid oxidation (HNO_3 treatment), sulfonation and sulfurization (CS_2 treatment). Figure 15 shows the effect of these pretreatment on mercury sorption. It is evident that both nitric acid oxidation and sulfonation improved the equilibrium sorptive capacity considerably. For CS_2 treated Giridih coal, both the intensity of sorption and equilibrium sorption capacity increased initially compared to untreated coal; however beyond an equilibrium concentration of 100 $\mu\text{g/l}$ of mercury the reverse was observed. The chemical changes of the coal surface as a result of these pretreatment and their consequent effects on mercury sorption are discussed as follows.

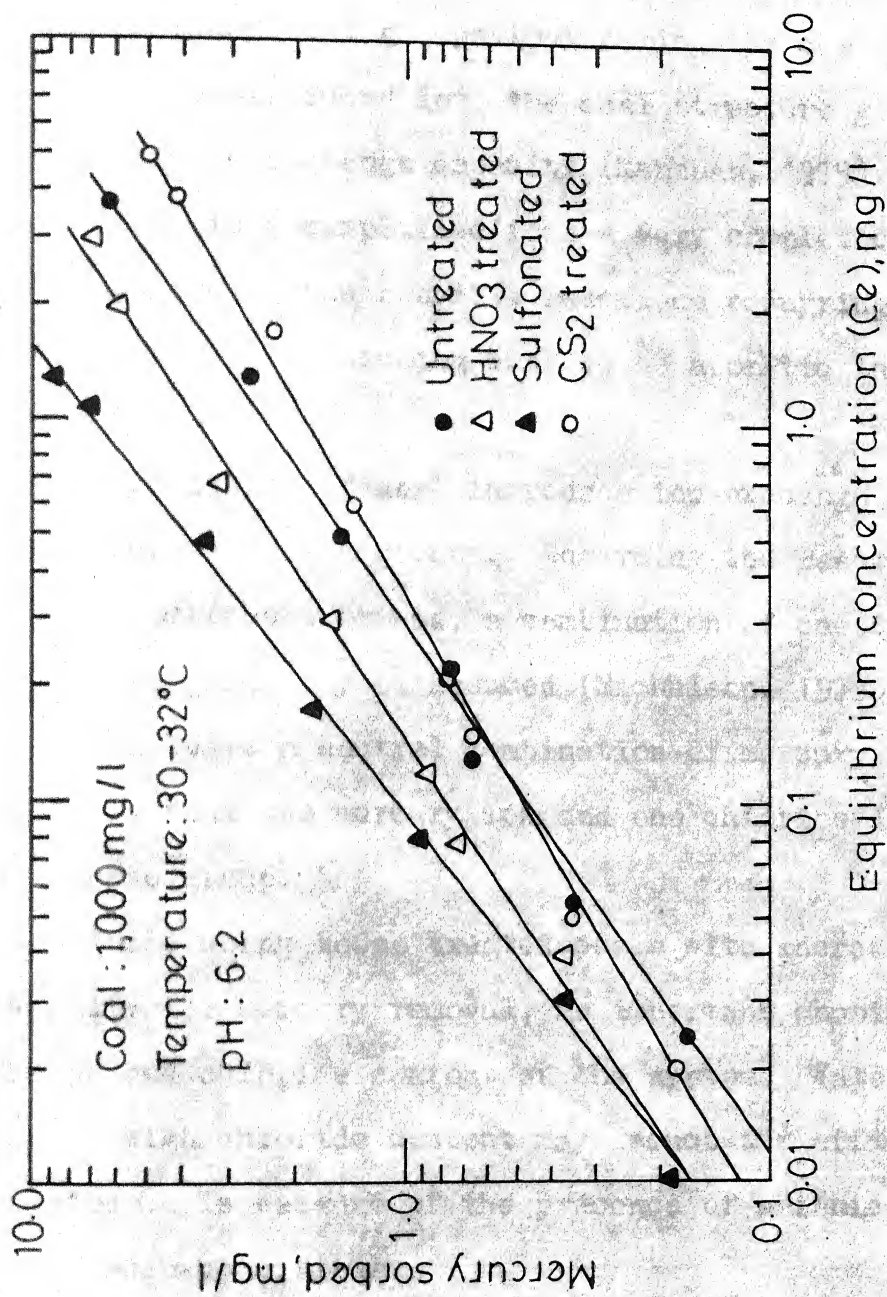


Fig. 15 - Linearised Sorption Isotherms for Giridih Coal with and Without Various Pretreatment.

Through the nitric acid oxidation process carboxyl and phenolic functional groups lost during the coalification process could be reintroduced into the coal structure giving it an increased ion-exchange capacity (Manahan, 1975). With an attempt to explain in a simplified form a very complex chemical interaction, some of the possible reactions occurring in this process are hypothesised assuming coal to be aromatic in character (Fig. 16).

Sulfonation of coal increases ion-exchange capacity by imparting sulfonate groups. Regarding the reaction between mercury and the sulfonate groups, a combination of one mercury atom per sulfonate group may be assumed (Michelson, 1975). This assumption does not leave a neutral combination of mercury ion and it is most probable that one mercury ion and one chlorine ion is added to each sulfonate group.

While using these treated coals with increased ion-exchange capacity for mercury removal, an important consideration may be the pH and chloride content of the system. Waters with high pH and/or high chloride content may reduce the efficiency of these treated coals because of the presence of anionic mercury species under such conditions.

Sulfurization of coal by carbon disulfide possibly forms certain chelating groups on the coal surface, e.g., xanthates, dithiocarboxylates or dithiocarbomates as indicated in the case of activated carbon by Humenic and Schnoor (1974). These chelating groups improve mercury binding. However, the reasons for the

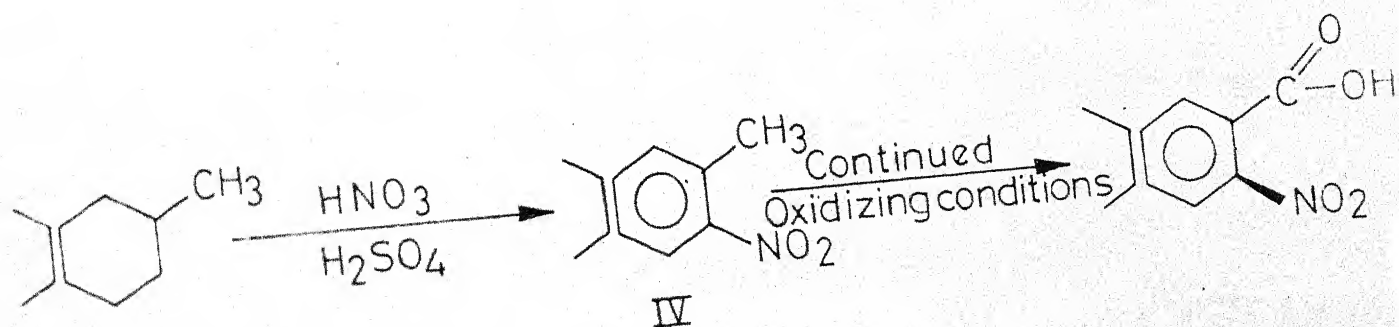
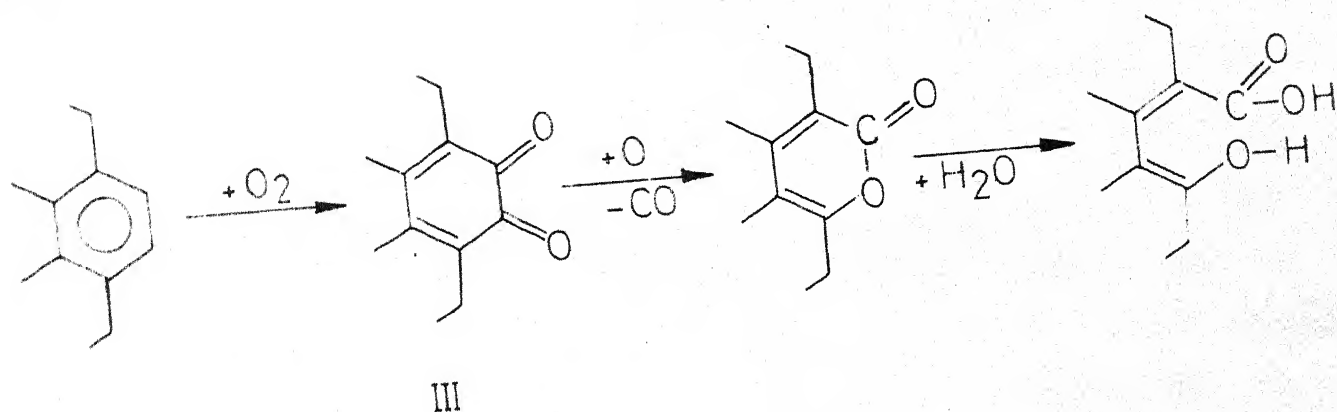
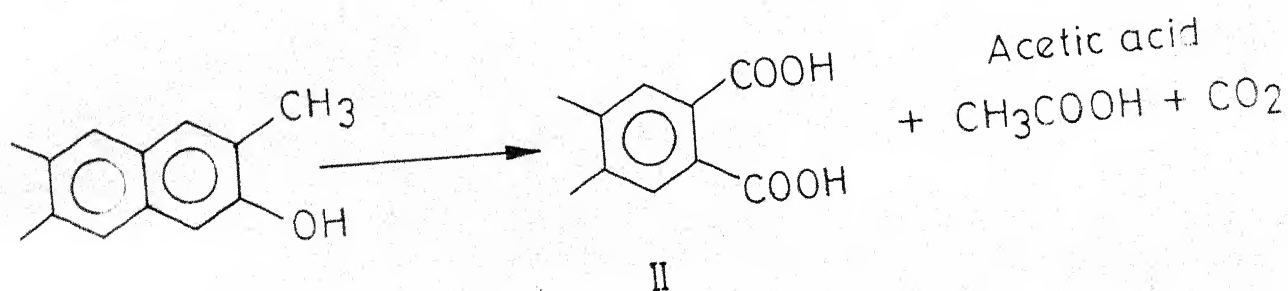
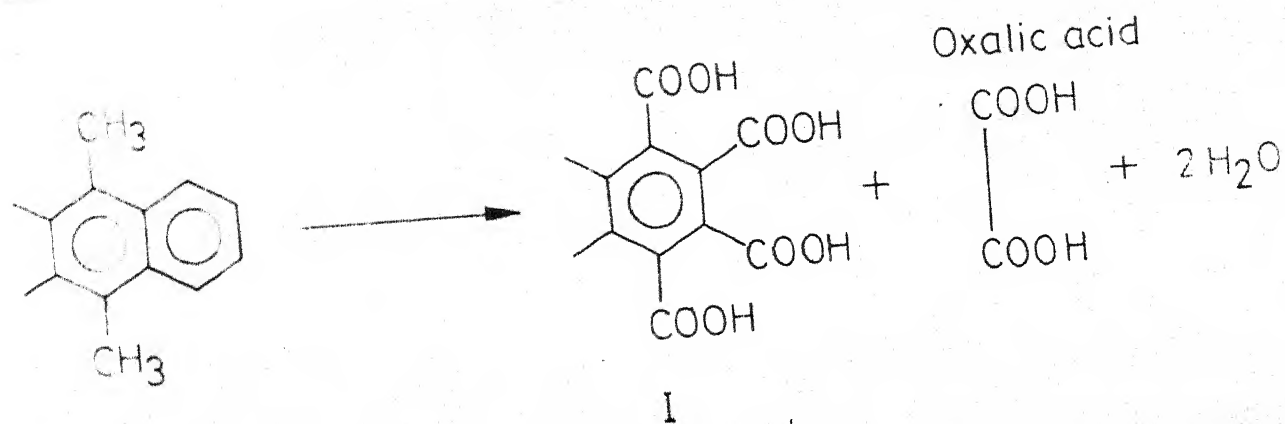


Fig. 16 - Reactions Involved During Nitric Acid Oxidation of Coal.

peculiar behaviour of the carbon disulfide treated coal beyond an equilibrium mercury concentration of $100 \mu\text{g/l}$ (Fig. 15) are not readily apparent. More detailed studies are necessary in this area.

8. Desorption and Regeneration

The kinetics of mercury desorption from mercury loaded Giridih coal using glass-distilled water is presented in Fig. 17. Similar to the sorption kinetics data, desorption data also exhibited a first order reversible kinetics. However, it is observed that the rate of desorption was lower and the equilibrium was attained only after 48 hr. The desorption of mercury at equilibrium was only 2 mg/g of coal, i.e., 18 percent of the loading.

Cycles of regeneration and loading of the Giridih coal-mercury system was investigated in terms of practical applications (Fig. 18). Sodium chloride and hydrochloric acid were selected as regenerants because it was observed earlier that mercury sorption decreased in presence of chloride. Also these are commonly used regenerants for ion-exchangers. It is evident from Tables 10-13 that both these regenerants were effective. Mercury recovery in the first regeneration cycle by 1 N hydrochloric acid was 8.5 mg and in the case of 0.2 N sodium chloride it was 7.3 mg . In the next cycle mercury recovery by both these regenerants were comparable and in the subsequent cycles, 0.2 N sodium chloride regenerant performed better by providing higher recovery and lower loss in loading capacity. In the case of regeneration with 0.1 N sodium chloride, the loss in loading capacity was fairly comparable with that observed with 0.2 N sodium chloride but the recovery of mercury was

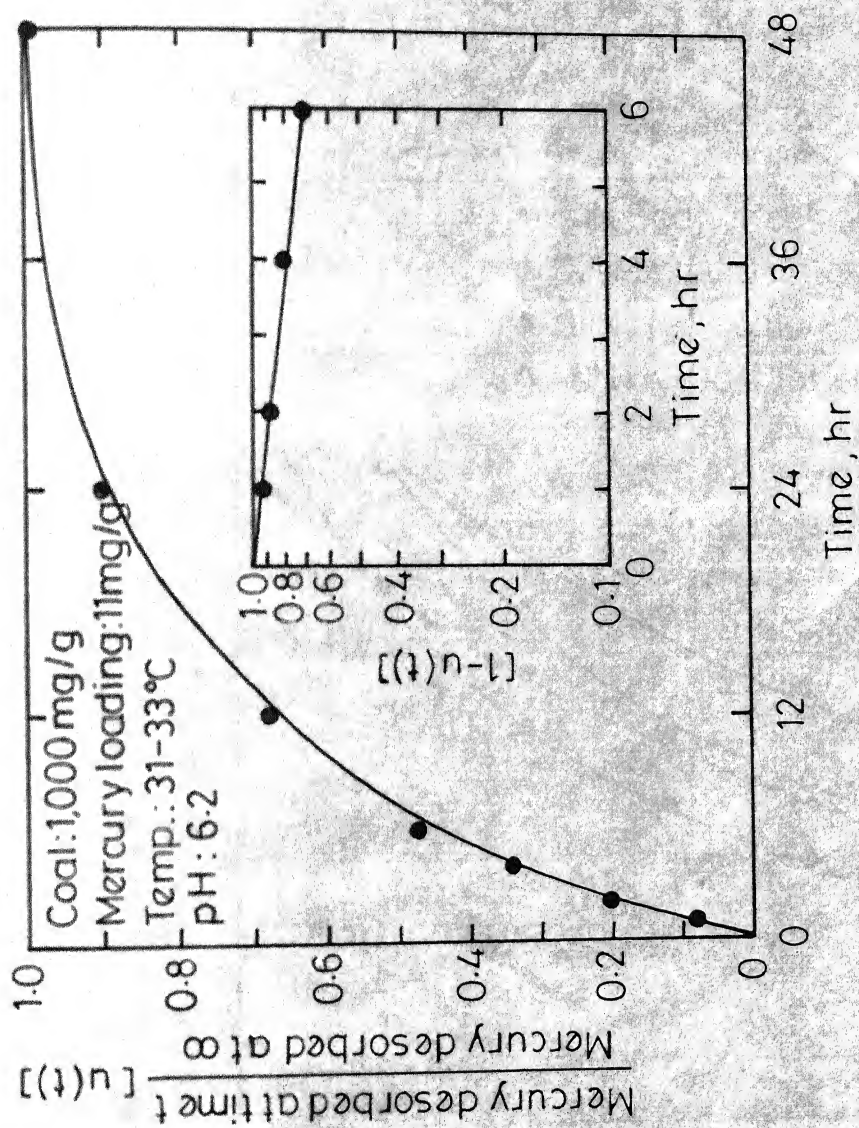


Fig. 17 - Desorption of Mercury from Loaded
 Giridih Coal.

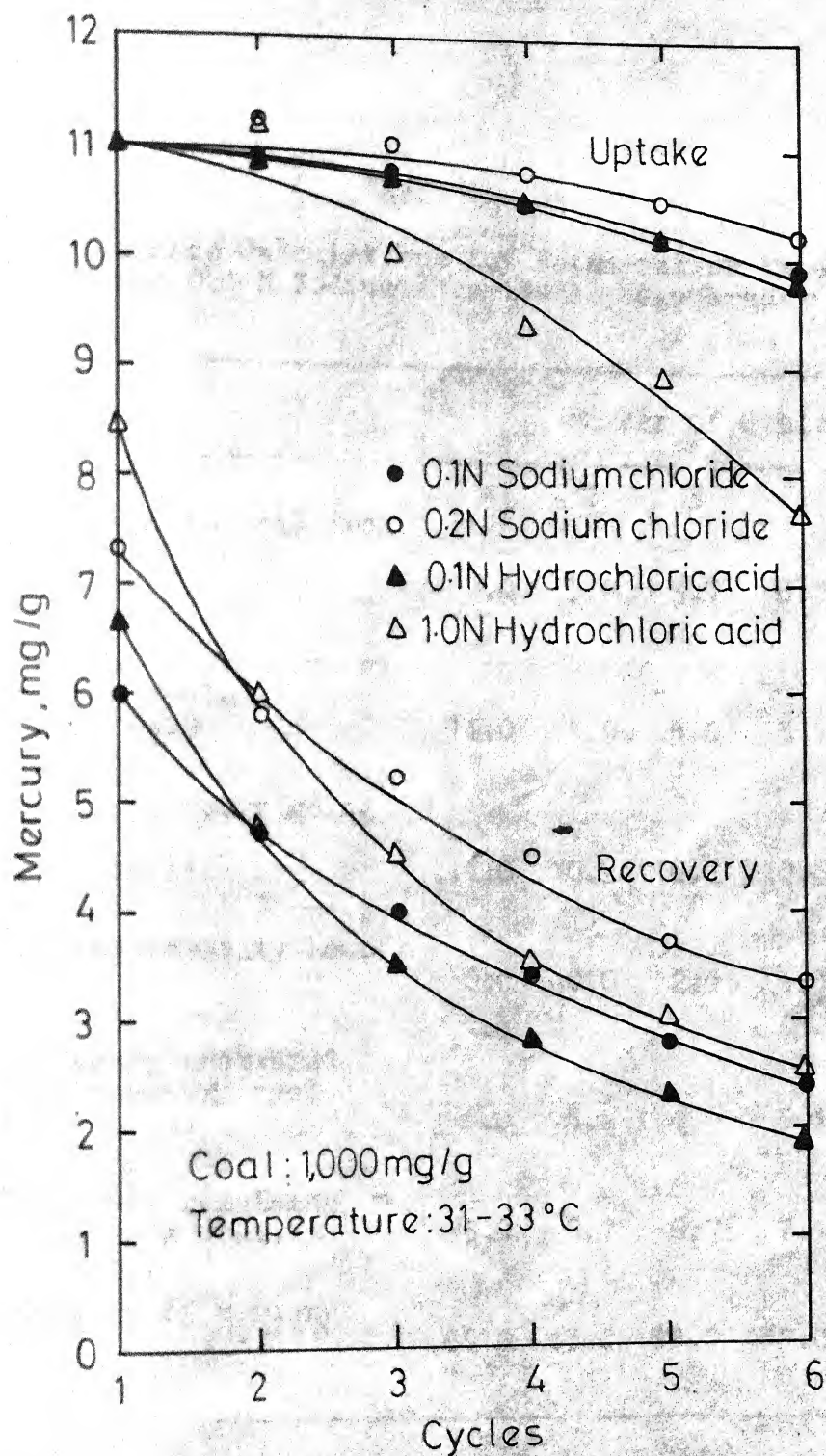


Fig. 18 -Regeneration of Giridih Coal.

Table 10

Material Balance Calculations for Regeneration Experiments
Using 0.1 N Sodium Chloride as Regenerant

	Number of Cycles					
	1	2	3	4	5	6
Amount of mercury in coal from previous recovery cycle (mg mercury/g coal)	0.0	5.0	5.7	6.75	7.1	7.4
Amount of mercury picked up by coal in loading cycle (mg mercury/g coal)	11.0	5.9	5.0	3.75	3.1	2.5
Total amount of mercury going into recovery cycle (mg mercury/g coal)	11.0	10.9	10.7	10.50	10.2	9.9
Percent loading capacity lost (%)	0.0	0.0	2.25	4.50	7.3	9.0
Amount of mercury recovered from coal in recovery cycle (mg mercury/g coal)	6.0	5.2	4.0	3.40	2.8	2.4
Amount of mercury remaining on coal (mg mercury/g coal)	5.0	5.7	6.75	7.10	7.4	7.5
Percent recovery of mercury from coal (%)	55.0	43.0	38.0	32.0	27.0	24.0

Table 11

Material Balance Calculations for Regeneration Experiments
Using 0.2 N Sodium Chloride as Regenerant

	Number of Cycles					
	1	2	3	4	5	6
Amount of mercury in coal from previous recovery cycle (mg mercury/g coal)	0.0	3.7	5.4	5.80	6.25	6.8
Amount of mercury picked up by coal in loading cycle (mg mercury/g coal)	11.0	7.5	5.6	4.90	4.30	3.4
Total amount of mercury going into recovery cycle (mg mercury/g coal)	11.0	11.2	11.0	10.75	10.50	10.2
Percent loading capacity lost (%)	0.0	0.0	0.0	2.25	4.50	7.3
Amount of mercury recovered from coal in recovery cycle (mg mercury/g coal)	7.3	5.8	5.2	4.50	3.70	3.3
Amount of mercury remaining on coal (mg mercury/g coal)	3.7	5.4	5.8	6.25	6.80	6.9
Percent recovery of mercury from coal (%)	66.0	52.0	47.0	42.00	35.00	52.0

Table 12

Material Balance Calculations for Regeneration Experiments
Using 0.1 N Hydrochloric Acid as Regenerant

	Number of Cycles					
	1	2	3	4	5	6
Amount of mercury in coal from previous recovery cycle (mg mercury/g coal)	0.0	4.3	6.2	7.2	7.7	7.9
Amount of mercury picked up by coal in loading cycle (mg mercury/g coal)	11.0	6.5	4.5	3.3	2.5	1.9
Total amount of mercury going into recovery cycle (mg mercury/g coal)	11.0	10.8	10.7	10.5	10.2	9.8
Percent loading capacity lost (%)	0.0	0.0	0.0	5.0	7.0	11.0
Amount of mercury recovered from coal in recovery cycle (mg mercury/g coal)	6.7	4.8	3.5	2.8	2.3	1.8
Amount of mercury remaining on coal (mg mercury/g coal)	4.3	6.2	7.2	7.7	7.9	8.0
Percent recovery of mercury from coal (%)	60.0	44.0	33.0	23.0	23.0	17.0

Table 13
Material Balance Calculations for Regeneration Experiments
Using 1.0 N Hydrochloric Acid as Regenerant

	Number of Cycles					
	1	2	3	4	5	6
Amount of mercury in coal from previous recovery cycle (mg mercury/g coal)	0.0	2.5	5.1	5.5	5.7	5.9
Amount of mercury picked up by coal in loading cycle (mg mercury/g coal)	11.0	8.7	4.9	3.9	3.0	1.7
Total amount of mercury going into recovery cycle (mg mercury/g coal)	11.0	11.2	10.0	9.4	8.7	7.6
Percent loading capacity lost (%)	0.0	0.0	9.0	15.0	19.0	31.0
Amount of mercury recovered from coal in recovery cycle (mg mercury/g coal)	8.5	6.1	4.5	3.7	2.8	2.5
Amount of mercury remaining on coal (mg mercury/g coal)	2.5	5.1	5.5	5.7	5.9	5.1
Percent recovery of mercury from coal (%)	77.0	54.0	45.0	37.0	34.0	33.0

sufficiently low in all the cycles. Therefore, among the four regenerants tested, 0.2 N sodium chloride appeared to be the most effective regenerant for the present system.

Low desorption of mercury (about 18 percent) from loaded Giridih coal with glass-distilled water conceivably represents the fraction rather loosely bound to the coal. It further indicates the possibility that a major fraction of the sorbed mercury binds to the coal probably through stronger interaction involving the surface functional groups of coal. Desorption in the range of 55-77 percent with sodium chloride or hydrochloric acid in the first regeneration cycle further substantiates this and represents the fraction sorbed by ion-exchange reactions. This is also supported by the presence of cationic species of mercury and carboxyl as well as hydroxyl groups on the coal surface which may take part in ion-exchange reactions. Significant recovery during regeneration also demonstrates the reversible nature of the sorption reaction. The fraction of the sorbed mercury not recoverable during regeneration presumably represents the mercury bound possibly through even stronger interaction, e.g., hydrogen bonding or chemisorption.

C. Nature of Mercury-Coal Sorption Interaction

At this stage of data presentation and analysis it appears appropriate to elaborate on the qualitative aspects of mercury-coal sorption interaction. An attempt is made in this section to present a coherent description of the interaction based on the

preceding discussions supported by further experimental data and evidence from the literature at appropriate places.

The mercury-coal sorption interaction may be viewed as a reversible first order temperature dependent reaction. This is demonstrated by the sorption kinetics data as well as significant desorption of the sorbed mercury with suitable regenerants. The first order reversible kinetic fit of the sorption data also indicates the possibility of an initial rapid reaction involving active sites existing on the external surface of coal with high affinity to mercury. This is followed by subsequent diffusion of mercury into coal for further reactions. Data to support this are being presented here using two different approaches:

- (i) A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half power of time rather than with time; nearly linear variation of the amount sorbed with half power of time is predicted for a large initial fraction of reactions controlled by rates of intraparticle diffusion (Crank, 1956). Figure 19 shows a linear relationship for the Giridih coal-mercury system when mercury sorbed is plotted against half power of time.
- (ii) Because the extent of surface reaction will vary with the available surface area, sorption rate should exhibit a monotonic increase with some function of the inverse of the diameter of the sorbent particles (Weber, 1972). For cases in which intraparticle transport controls the sorption rate,

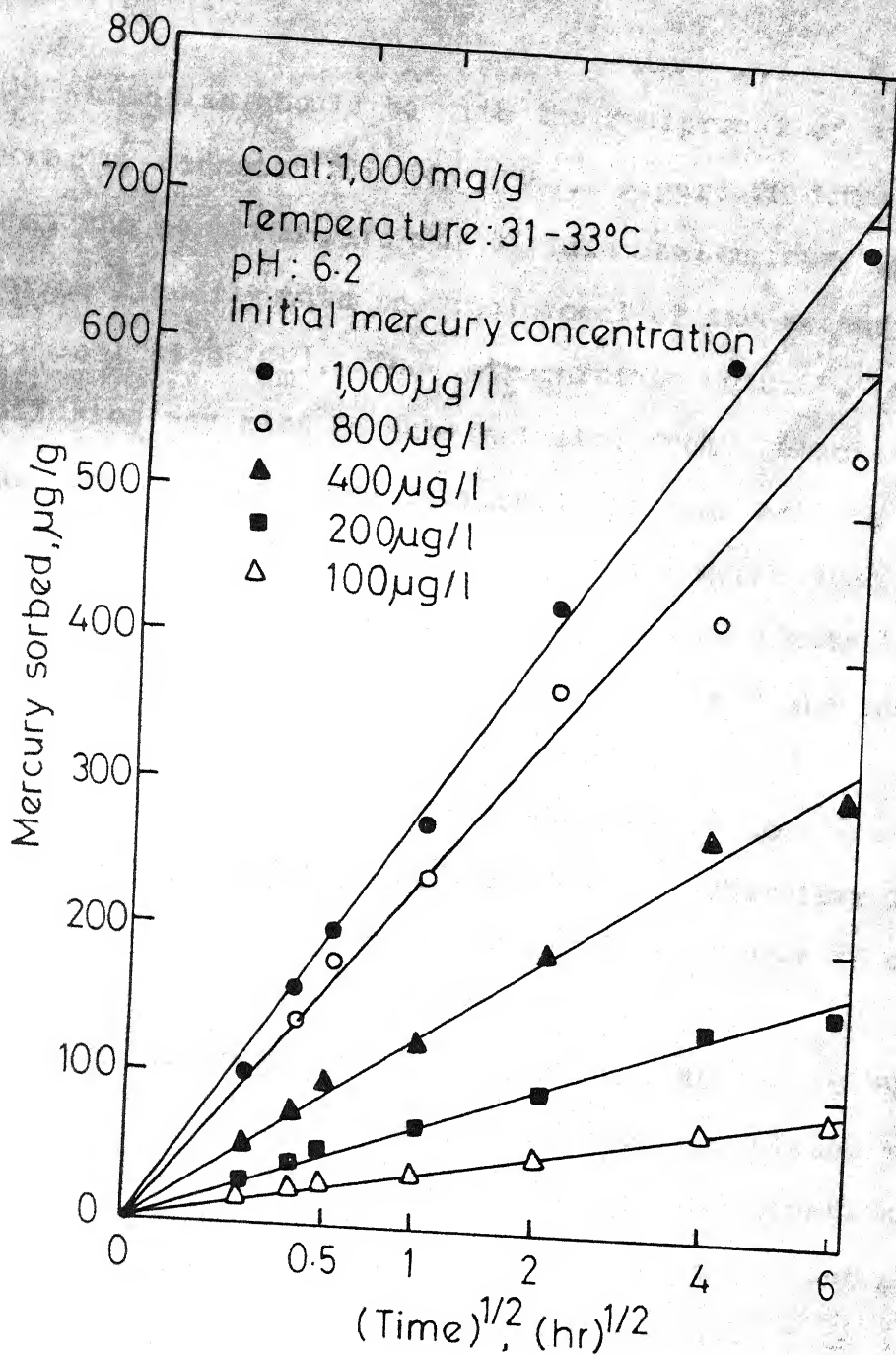


Fig. 19 -Plot of Mercury Sorbed vs. (Time)^{1/2} for Giridih Coal-Mercury System for Different Initial Mercury Concentration.

the variation should be with the reciprocal of some higher power of diameter (Crank, 1956). Figure 20 demonstrates that the sorption rate for Giridih coal-mercury system varies linearly with the reciprocal of the second power of the coal size (G_m). The intraparticle nature of mercury diffusion may also be substantiated from a consideration of the size of micro- and macropores of coal and the radius of mercury ion as well as the size of the mercury complexes. Micropores on coal are of the order of 25 \AA with many of the ultramicroscopic size (Chiche et al., 1967) and macropores are upto 200 \AA (Shannon and Silverston, 1968). The ionic radius of mercury ion is 1.01 \AA and the size of mercury complexes are upto 50 \AA (Silen, 1964). Therefore it appears reasonable that both the micro- and macropores of coal participate in mercury sorption.

Involvement of an appreciable activation energy (8.39 kcal/mole) is indicative of some specific interaction between the surface groups of coal and mercury, possibly a combination of several interactions which seems likely due to the heterogeneous nature of the coal surface. Desorption and regeneration data indicate an ion-exchange nature of the reaction apart from possible contribution due to even stronger reactions, e.g., hydrogen bonding and chemisorption. A discussion on the possible interaction between the surface functional groups of coal and mercury is presented using evidence from IR spectral studies and information available in the literature.

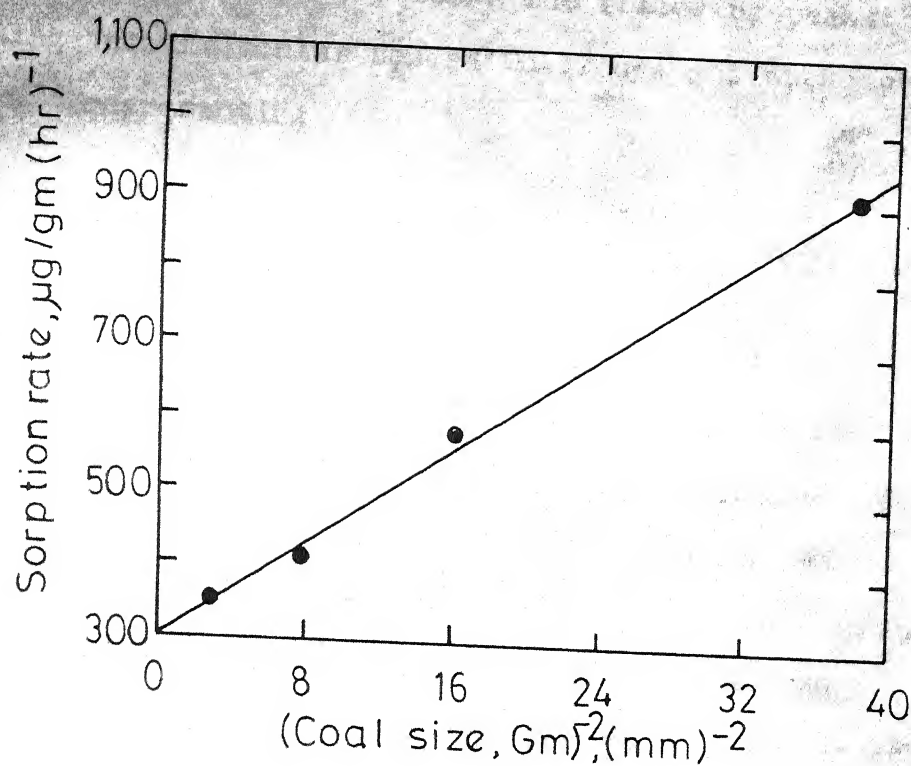
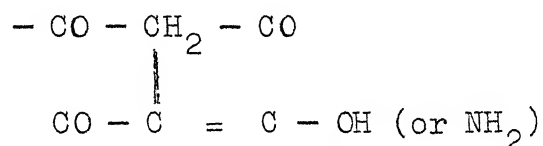


Fig. 20 -Effect of Giridih Coal Size on Mercury Sorption.

Figures 21 and 22 show IR spectra of Giridih coal and Giridih coal with sorbed mercury, respectively, using Nujol base. Large background absorption by carbon precluded sharp well defined spectra. The coal spectra shows the following peaks: (i) 2350 cm^{-1} revealing intramolecular bonded OH groups and phosphorous, (ii) 1600 cm^{-1} representing



groups, (iii) 1075 cm^{-1} ; C-O stretching of alcohols, linear and cyclic ethers (Brown, 1955), (iv) 900 cm^{-1} ; alkanes, such as tertiary butyl, carboxyl groups (COOH), primary amines, ($\text{CH}_2\text{-NH}_2$) and (CH-NH_2) and SH group, and (v) $790\text{ to }800\text{ cm}^{-1}$ aromatic C-H out of plane vibration frequencies observed in a number of single and condensed ring structures (Brown, 1955). The existence of the aforementioned groups on Giridih coal were also demonstrated by previous investigators (Oza, 1974 and Sriramulu, 1975). Presence of hydroxyl, carboxyl group is also suggested by Mukherjee (1978) based on the ultimate and proximate analyses of the coal. According to Mukherjee (1978) almost all the sulfur is present as organic sulfur on Giridih coal. This may be in sulfide or sulfhydryl form. The IR spectra of Giridih coal with sorbed mercury (Fig. 22) shows that the peaks at 2350 cm^{-1} and 900 cm^{-1} disappeared suggesting hydrogen bonding and interaction of mercury with sulfhydryl, carboxyl and amine groups.

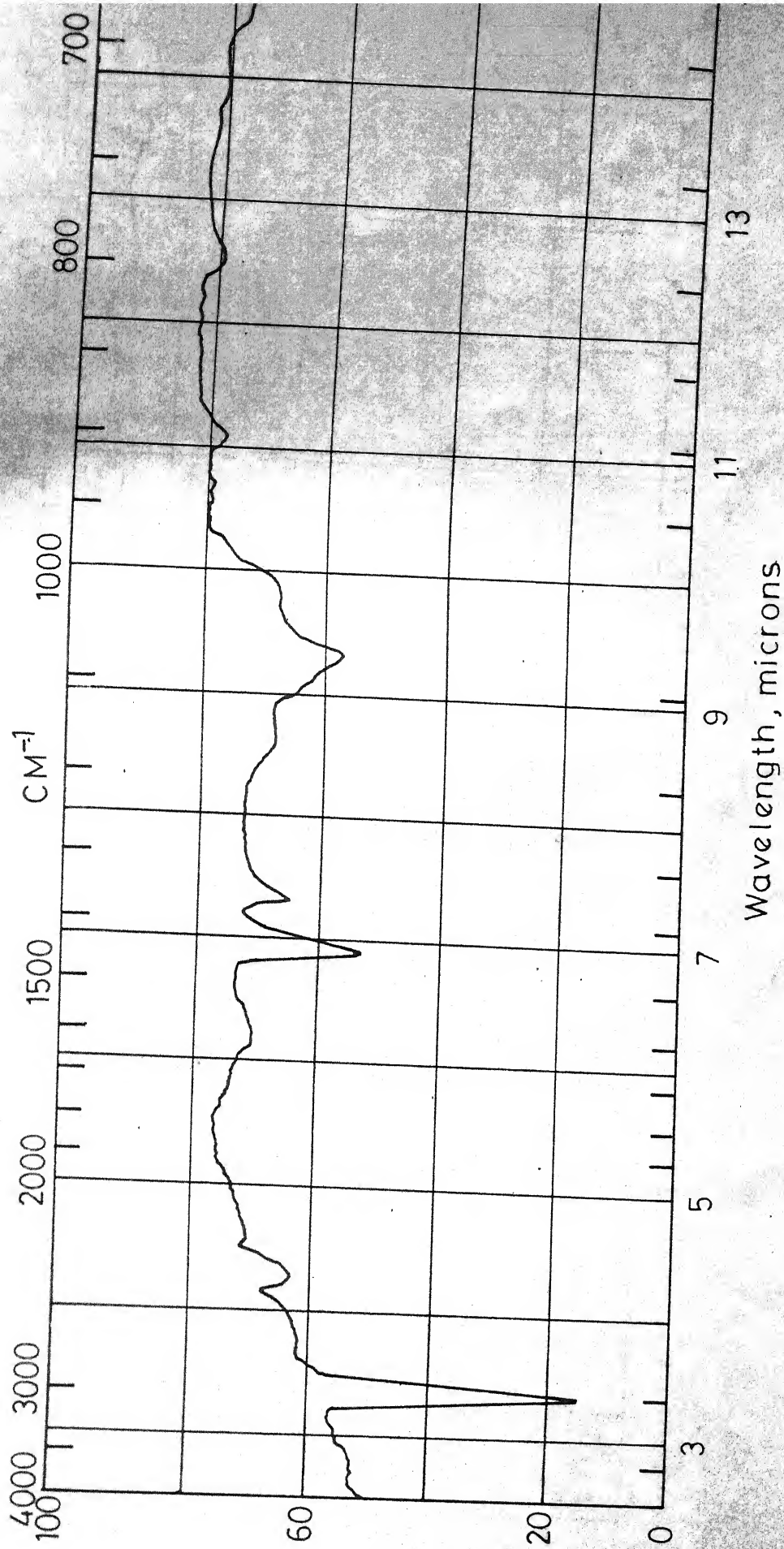


Fig. 21 - Infrared Spectra of Giridih Coal.

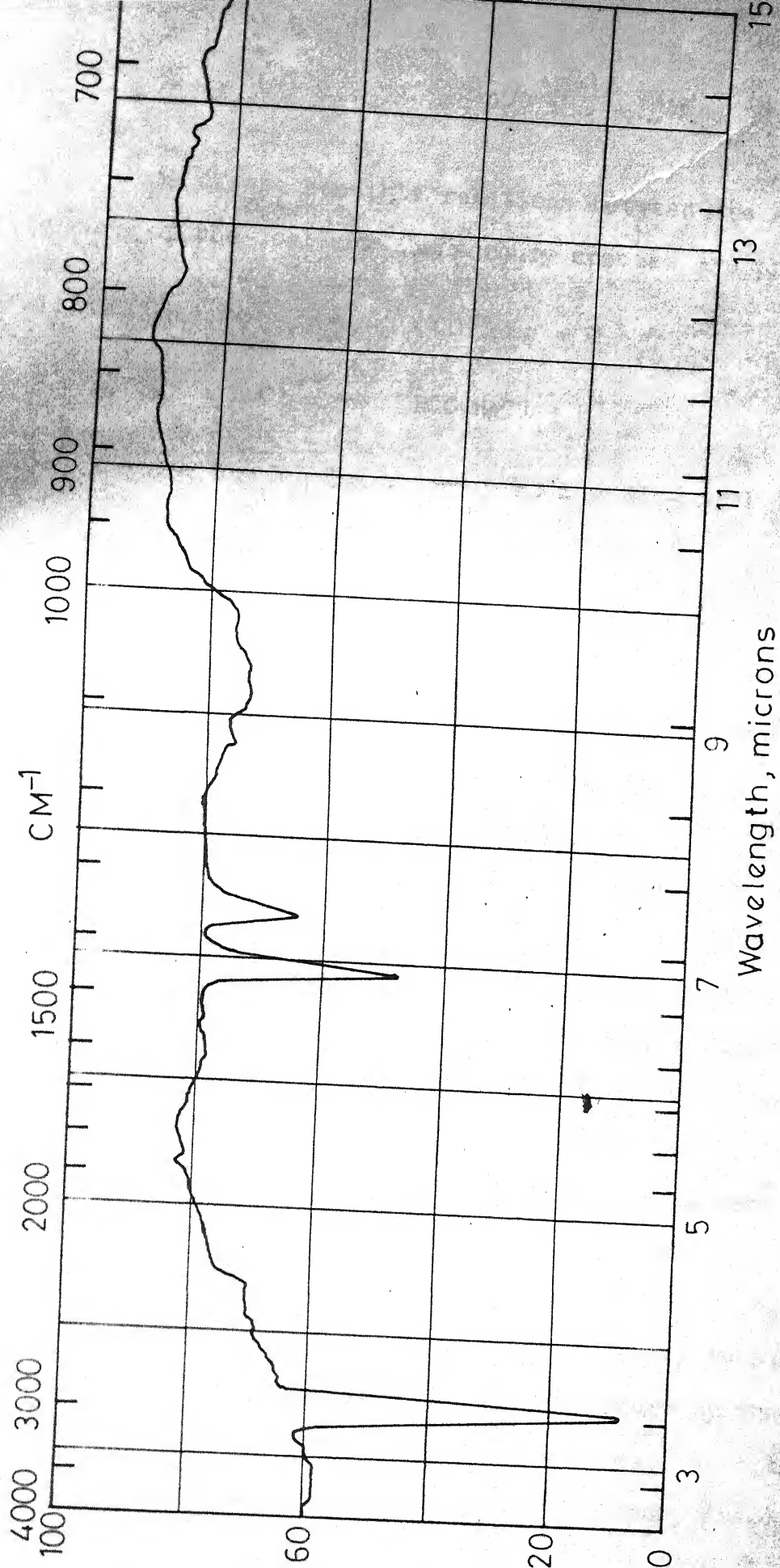
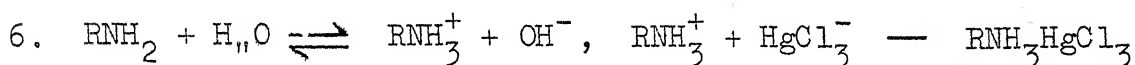
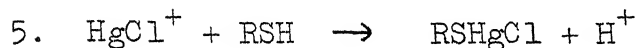
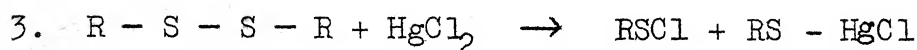
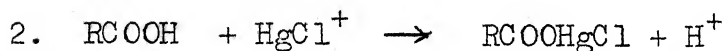


Fig. 22 - Infrared Spectra of Giridih Coal with Sorbed Mercury.

Some of the possible reactions between the surface functional groups of the coal and the mercury species are presented below.



D. Mercury Association with Turbidity

Before conducting continuous coal column studies on mercury removal, it was thought appropriate to investigate the degree of mercury association with the particles constituting turbidity and its consequences on mercury removal. Using an initial kaolinite turbidity in the range of 5-80 NTU, two methods were employed for removing turbidity, viz., coagulation with the optimum alum dose and centrifugation @ 6000xg for 10 min. It is seen from Fig. 23 that removal of mercury increased with initial turbidity and the trend of removal by two methods paralleled each other. However, slightly higher mercury removal by coagulation by alum was possibly due to increased trapping of mercury by the destabilised clay particles and the alum floc. It is also seen that the percent mercury removal as a result of mercury association with

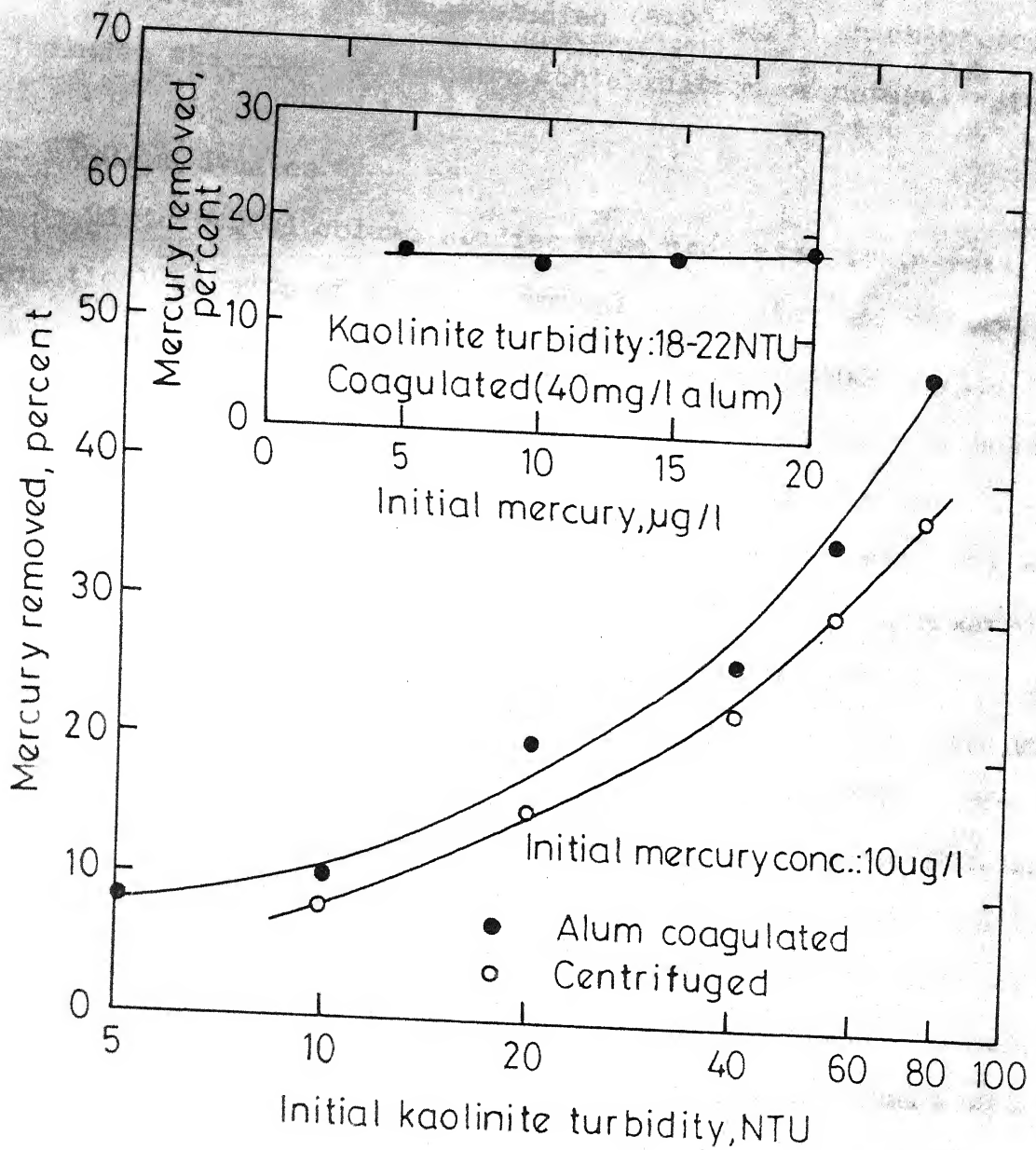


Fig. 23 - Effect of Turbidity and Mercury Concentration on Mercury Removal in Association with Turbidity.

turbidity did not depend significantly on the initial mercury concentration in the range studied (5-20 $\mu\text{g/l}$) which probably includes the range of mercury contamination of natural waters.

E. Column Studies

Giridih coal column studies were conducted to investigate the practical aspects of mercury removal from water and wastewater using mercury concentration in the range of 10-2000 $\mu\text{g/l}$. Figure 24 shows the performance of a 45 cm deep coal column with initial mercury concentration of 10 $\mu\text{g/l}$ which probably includes the range of mercury concentration of natural waters. When mercury was present in turbidity-free tap water, the coal column removed about 60 (run 1) and 80 (run 2) percent of the input mercury at flow rates of 12.8 and 6.4 ml/min, respectively. However, when mercury was present in association with turbidity of 18-22 NTU (run 3) coagulation with 40 mg/l alum (optimum dose) produced residual mercury and turbidity levels of about 8 $\mu\text{g/l}$ and 1 NTU, respectively which was the influent to coal column. The mercury level in the column effluent of this run at 6.4 ml/min ranged between 1.0-1.5 $\mu\text{g/l}$. These runs demonstrate that through treatment with coal it is possible to achieve a level of mercury in the treated water corresponding to the range of permissible mercury concentration (1-2 $\mu\text{g/l}$) of drinking water.

Figure 25 shows mercury removal from turbidity-free tap water by Giridih coal column with initial mercury concentrations of 400 and 2000 $\mu\text{g/l}$. These higher mercury concentrations were selected

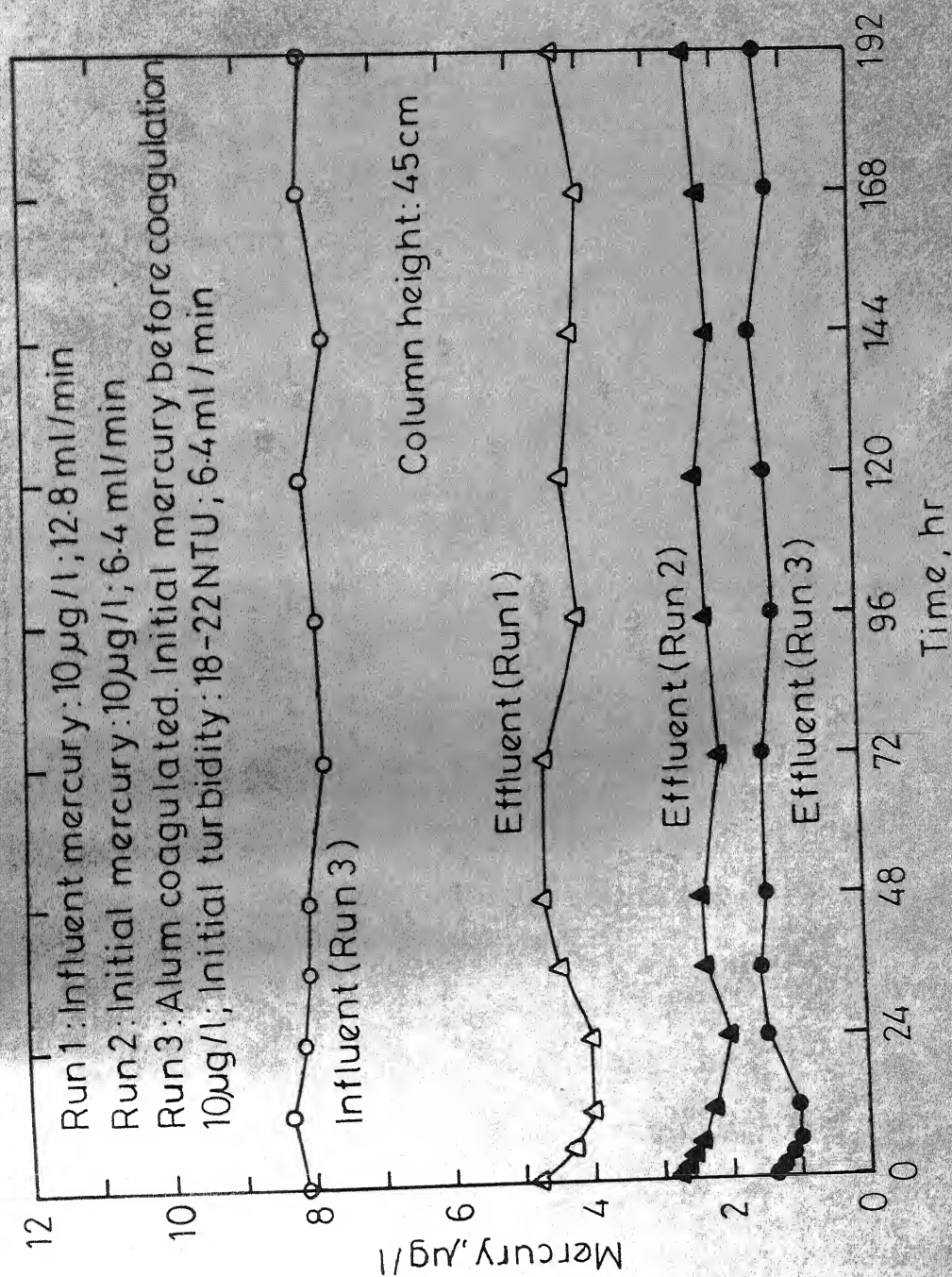


Fig. 24 - Mercury Removal by Giridih Coal Column (Low Concentration).

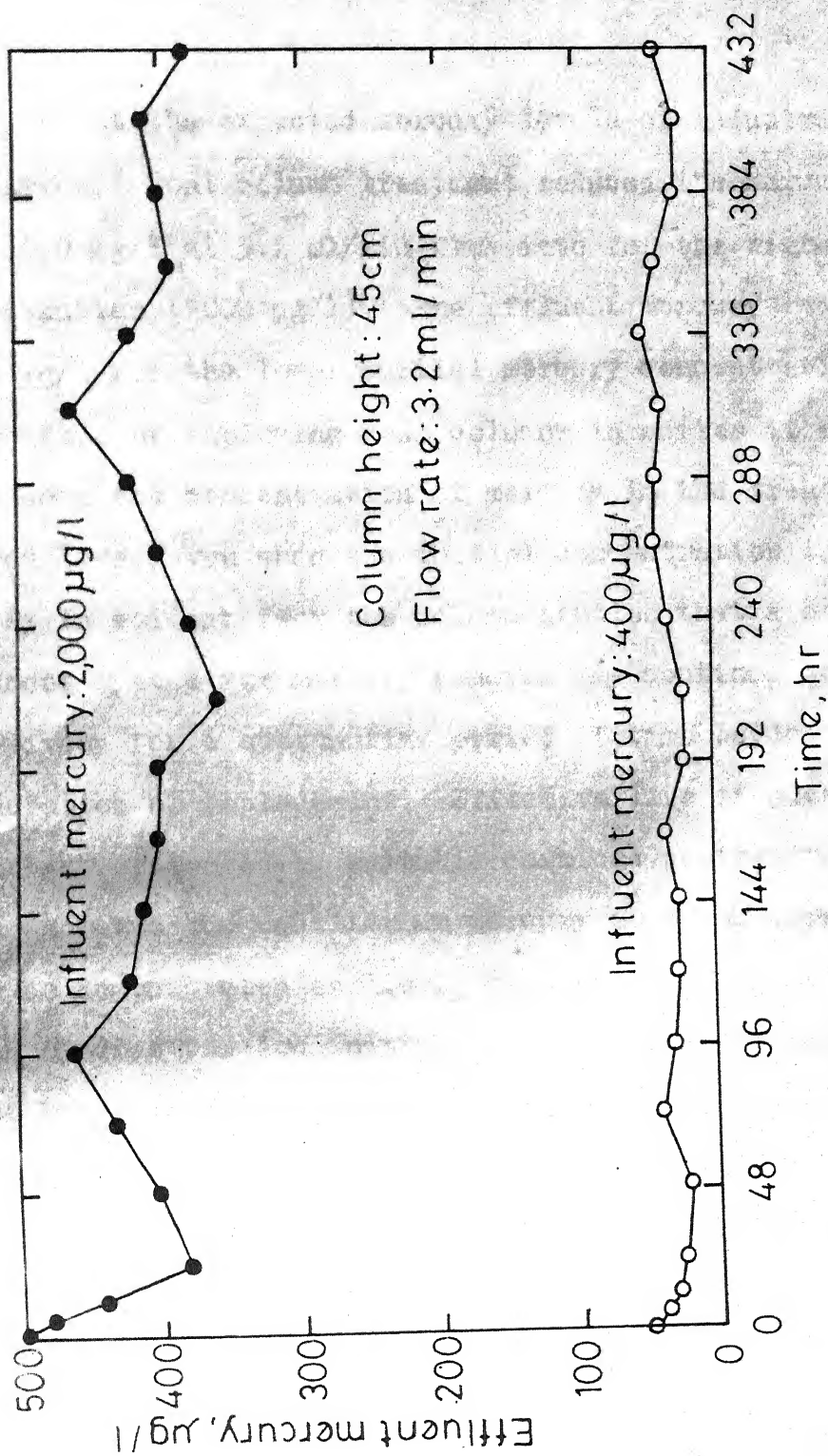


Fig. 25 - Mercury Removal by Giridih Coal Column.
(High Concentration)

to represent the expected mercury levels of industrial waste discharges. Coal column treatment reduced the mercury level to about 400 $\mu\text{g/l}$ at 3.2 ml/min flow rate for the higher initial concentration (2000 $\mu\text{g/l}$). The effluent mercury ranged between 25-50 $\mu\text{g/l}$ for the lower initial mercury concentration (400 $\mu\text{g/l}$). Apparently, by employing coal columns in series it is possible to bring down the concentration of mercury in the treated water to any desired level even when the initial concentration is very high.

It is evident from the column studies that a coal based treatment system for mercury removal may continue to perform effectively for a substantial period of time before needing regeneration or replacement. Effective life of such a system may be further prolonged by suitable chemical pretreatment of the coal which improves the equilibrium mercury sorption capacity of the media as demonstrated earlier. The contact times in the present column studies for low initial mercury concentration (Fig. 24) were in the range of 2.8-5.6 min which is comparable to the suggested contact time for mercury removal by activated carbon (3.5 min) with similar initial mercury concentration (10 $\mu\text{g/l}$) (Gary and James, 1973). The contact time used for high initial mercury concentration (Fig. 25) was 11.4 min which is rather high compared to a minimum recommended contact time (6 min) for activated carbon column treatment of mercury confining caustic waste (Smith et al., 1971).

VI. SUMMARY AND CONCLUSIONS

It has been shown that bituminous coal is effective in removing mercury from water and wastewater. Using Giridih bituminous coal, batch sorption kinetics of inorganic mercury were described by a first order reversible reaction and sorption equilibria by the Freundlich equation. Mercury sorption was temperature dependent and the average values of heat of sorption and activation energy being 0.91 and 8.39 kcal/mole, respectively. The ultimate equilibrium mercury sorptive capacity at pH 6.2 was observed to be 11 mg/g of coal (G_m 357 μ m) at 31-33°C. Mercury sorption reduced with increase in pH and the rate increased with increase in mercury concentration. Chemical environment also influenced mercury sorption. Presence of chloride or calcium in the system reduced the equilibrium sorptive capacity. Chemical pretreatment of coal like nitric acid oxidation, sulfonation, and sulfurization improved sorption efficiency due to the resulting modification of the coal surface groups.

The nature of the sorption kinetics data indicated a rapid interaction involving mercury species and the active sites on the external surface of the coal followed by a comparative slower intraparticle diffusion. This was corroborated through a consideration of the sizes of the micro- and macropores of coal and the mercury species. Linear variation of the rate of sorption with the sorbent size and mercury sorption with the half power of time provided further experimental evidence of this effect.

Desorption and regeneration data of mercury loaded coal indicated ion-exchange nature of the sorption reactions apart from possible contribution due to even stronger interactions, e.g., hydrogen bonding and chemisorption. Involvement of high energy of activation also indicated such interactions. On the basis of the presence of functional groups on the coal surface evidenced from IR spectral studies, ultimate and proximate analyses of coal and literature data, a discussion has been presented on the possible interaction between mercury and these functional groups.

Downflow coal column was found effective in treating input mercury levels in the range of 10-2000 $\mu\text{g/l}$. When mercury (10 $\mu\text{g/l}$) was present with turbidity, column treatment preceded by alum coagulation and sedimentation produced effluent mercury concentration in the range of 1.0-1.5 $\mu\text{g/l}$ at a flow rate of 6.4 ml/min. Mercury (10 $\mu\text{g/l}$) in turbidity-free water was reduced by 60 and 80 percent at flow rates of 12.8 and 6.4 ml/min, respectively. The coal columns were effective for a substantial period of time without any need for regeneration or replacement.

Based on the findings of this investigation using Giridih bituminous coal following conclusions may be drawn.

- (i) Mercury sorption on coal is a first order reversible reaction and sorption isotherm follows Freundlich equation. Sorption is temperature dependent and reduces with increase in pH.

- (ii) Chemical environment influences mercury sorption and the mercury rate increases with mercury concentration. Presence of chloride and calcium reduces mercury sorption.
- (iii) Chemical pretreatment of coal like nitric acid oxidation, sulfonation, and sulfurization improves sorption efficiency possibly through resulting modification of the coal surface groups.
- (iv) Mercury sorption on coal is an intraparticle transport phenomenon.
- (v) Mercury-coal sorption interaction is of the nature of an ion-exchange reaction with possible contribution of even stronger interactions, e.g., hydrogen bonding and chemisorption.
- (vi) Sodium chloride and hydrochloric acid are effective regenerants for coal-mercury system.
- (vii) A process based on coal sorption is effective in the treatment of a wide range of initial mercury concentration. Pretreatment for turbidity removal when included in such a process removes considerable fraction of mercury due to its association with the turbidity.

VII. ENGINEERING SIGNIFICANCE

The most significant aspect of this present study is the investigation of the potential of indigenous bituminous coal in removing mercury from water. Furthermore, an understanding of the mercury-coal sorption interaction and the relevant parameters affecting mercury sorption on coal will also help evolve criteria for design of a coal sorption process on a sound, economical, realistic and rational basis. A long-felt need in search of a cheap, economical and practical sorbent for removing mercury has been probably satisfied. The removal of mercury from water and wastewater becomes extremely important due to increasing number of industries using mercury and thus loading our water resources with this toxic contaminant.

To have a completely separate unit for mercury removal may not be an economically feasible and practical approach for treating mercury contaminated raw water supplies. More desirable would be a process which can easily be incorporated in the already existing treatment units without affecting their performance and involving huge expenses. It is expected that the present study will be able to satisfy this requirement. Existing filter units may be converted to coal-sand dual-media filter to enhance mercury removal apart from other added advantages inherent to sand filters. The concentration of mercury in raw water usually used for public water supply is normally low. The observed ultimate capacity of coal will be able to take care of mercury removal

in a dual-media coal-sand filter for a reasonable length of time without affecting the performance and needing frequent regeneration or replacement. In case of any slug discharge of mercury into the raw water source use of powdered coal before the coagulation unit would probably trap a major fraction of the mercury load and this mercury in association with turbidity will be removed in the subsequent processes. For industrial wastewater containing higher mercury concentration, series of coal sorption columns would probably be able to bringdown the mercury level in the effluent to the desired concentration of discharge.

Regeneration of the exhausted coal columns with rather inexpensive chemicals like sodium chloride and hydrochloric acid adds another plus point to the coal sorption process for removing mercury. In addition, coal being easily available and requiring no elaborate processing or pretreatment makes it an attractive material for such a process.

VIII. SUGGESTIONS FOR FUTURE WORK

On the basis of the results of the current study it is felt that further investigation should be pursued in the following areas:

- (1) A parametric evaluation of the coal filter in the removal of mercury from water should be undertaken. This is important since quantitative extrapolation of batch data to column operation is difficult probably because of hydrodynamic and other parameters of relevance in filtration.
- (2) In order to predict mercury sorption by various coals and to gain further understanding of mercury-coal sorption interaction more precise qualitative and quantitative evaluation of the surface groups on coal should be carried out.
- (3) Inexpensive and practical methods of incorporating the desired surface groups on the coal surface for improving mercury sorption should be investigated.
- (4) Studies on the removal of mercury from industrial wastewaters having high concentration of chloride may be undertaken by incorporating certain anionic exchange groups on the coal surface.
- (5) Role of inorganic and organic turbidity particles in trapping mercury and consequent mercury removal in association with should be investigated in greater details

This knowledge may be effectively used for enhancing mercury removal using conventional water treatment processes.

- (6) An attempt should be made to study the feasibility of recovering mercury during regeneration of the spent coal.
- (7) Potential of coal in removing other heavy metals may be explored.

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